PHOSPHORUS REDUCTION IN DAIRY EFFLUENT THROUGH FLOCCULATION AND PRECIPITATION

A Thesis

by

AMANDA BRAGG

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2003

Major Subject: Soil Science

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Approved as to style and content by:

Kevin McInnes (Chair of Committee)	Jennifer McGuire (Member)
Sam Feagley (Member)	Mark Hussey (Head of Department)

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ABSTRACT

Phosphorus Reduction in Dairy Effluent Through Flocculation and Precipitation.

(December 2003)

Amanda Bragg, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Kevin McInnes

Phosphorus (P) is a pollutant in freshwater systems because it promotes eutrophication. The dairies in the North Bosque and its water body segments import more P than they export. Dairies accumulate P-rich effluent in lagoons and use the wastewater for irrigation. As more P is applied as irrigation than is removed by crops, P accumulates in the soil. During intense rainfall events, P enters the river with stormwater runoff and can become bio-available. Reducing the P applied to the land would limit P build up in the soil and reduce the potential for P pollution. Since wastewater P is associated with suspended solids (SS), the flocculants, poly-DADMAC and PAM, were used to reduce SS. To precipitate soluble P from the effluent, NH_4OH was added to raise the pH. Raw effluent was collected from a dairy in Comanche County, TX, and stored in 190-L barrels in a laboratory at Texas A&M University. Flocculant additions reduced effluent P content by as much as 66%. Addition of NH_4OH to the flocculated effluent raised the pH from near 8 to near 9, inducing P precipitation, further reducing the P content. The total P reduction for the best combination of treatments was 97%, a decrease from 76 to 2 mg L^{-1}. If this level of reduction were achieved in dairy operations, P pollution from effluent application would gradually disappear.

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CHAPTER I

INTRODUCTION

As population increases, the quantity and quality of water resources have become the focus of many debates and studies. Limiting runoff and leaching of nutrients supplied for plant nutrition is a major concern of policymakers pushing for clean water resources and sustainable agricultural systems. The impacts of excess nutrients on water quality have been well documented (Loehr, 1974b; Barker et al., 1994; Daniel et al., 1994; Correll, 1998; Sharpley et al., 1998; Sims et al., 1998; Edwards et al., 2000). Simple solutions to prevent pollution have been difficult to come by because the chemistry and flow pathways of phosphorus (P) and nitrogen (N) cause strategies to manage P to conflict with best management practices for N control (Heathwaite et al., 2000). In fact research shows that land applications at the agronomic N-rate (a common nutrient management practice used for biosolids) results in accumulation of soil P in excess of crop P uptake (Kelling et al., 1977; Maguire et al., 2000)

Phosphorus (P) has been identified as the limiting nutrient for algal growth in most freshwater systems, and when excessive additions of P enter water bodies, algal blooms result (Loehr, 1974b). Over two hundred million tons of P are discharged into national surface waters each year (Leedan et al., 1990). In freshwater systems such as rivers, runoff from animal farms where nutrients have accumulated is generally linked to eutrophication

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downstream (Jaworski et al., 1992). Although wastes from confined animal feeding operations (CAFOs) are a potentially recyclable source of plant nutrients and a raw material for energy production, the maximum potential for hastened eutrophication usually occurs in watersheds with intensive CAFO manure production (Council for Agricultural Science and Technology, 1996; USDA and USEPA, 1998). In the upper North Bosque and North Bosque River water body segments of Central Texas, P pollution of streams and reservoirs is a problem (Texas Water Commission and Texas State Soil and Water Conservation Board, 1991). The dairy farms located upstream are perceived to be main sources of the P (McFarland and Hauck, 1999). Undesirable algal growth in Lake Waco, which supplies the city of Waco and surrounding areas with drinking water, has put the city at odds with upstream dairy farmers.

In areas of intensive agriculture, P surpluses result from more P being imported in feedstuff and fertilizer than exported in produce (National Research Council, 1993; Tunney, 1988). The mean number of cows per dairy operation has increased from 37 to 87 over the last two decades while the amount of land per operation has increased little (USDA National Agricultural Statistics Service, 20001). Consequently, the amount of land available per cow for waste application has decreased (Kashmanian, 1994). Effluent from dairies has nutritional value for plant growth, but it often has been applied to land in quantities greater than plant uptake. This excess effluent application has led to a buildup of nutrients in the soil surface, particularly P. A typical N:P ratio on for dairy manure is 2:1, and 5.5:1 is a typical N:P ratio for a dairy effluent (Sanderson et al., 2001). Effluent and manure are most often applied at a rate for N uptake, which results in a buildup of P in the soil (Sweeten and Wolfe, 1993).

In this setting P pollution of water resources begins when rainstorm intensities are such that water runs off fields where P has built up in the soil surface over years of excess

application. Phosphorus leaves the field associated with or attached to eroded soil particles or dissolved in the runoff water. Phosphorus then enters the river and stimulates algal growth therein and in downstream water bodies. Phosphorus available for algal growth, considered bioavailable P (BAP), is often fractionated into two types: soluble P and particulate P (Haygarth and Sharpley, 2000). Reducing P concentrations in the effluent from dairies to concentrations low enough that plants could remove it along with the N consumed would limit buildup in the soil and reduce pollution of surface waters. Reducing concentrations to levels where total P applied as effluent is below crop or pasture requirements would result in plants mining P from overloaded soils. Reduction of P concentrations prior to entering the lagoon would also decrease the potential for P pollution caused by lagoon overflow.

CHAPTER II

LITERATURE REVIEW

Background

The association between P additions to water bodies and eutrophication of those water bodies is well documented (Carpenter et al., 1998; Correll, 1998; Foy and Watts, 1998; Parry, 1998). Loehr (1974b) found undesirable aquatic weed growth occurred in water bodies with excessive additions of P. Algal growth in fresh water systems is often limited by the amount of P that is bioavailable because P is a strictly geological element with no atmospheric inputs (Schindler, 1977). Phosphorus enrichment of waters and the consequential algal blooms produce environmental problems such as emission of obnoxious odors, foul tasting water, and fish kills. These problems lead to a decrease in recreational value and an increase in expense of necessary treatment of water resources (TNRCC, 1999).

Phosphorus pollution is a problem in the upper North Bosque and North Bosque River waterbody segments. The Texas Natural Resource Conservation Commission (TNRCC, 1999) estimated that over 200,000 people use water originating in the North Bosque River as their primary drinking source. Although the water bodies associated with North Bosque River in central Texas have several sources of P, including carry-over from municipality wastewater treatment plants, overflow of the effluent lagoons and runoff from waste application fields have been targeted as the primary source (Sweeten and Wolfe, 1993). To prevent lagoon overflow, effluent is irrigated from the lagoon onto fields. The dairies in this watershed import more P in feed stuffs than they export in milk products, thus as the effluent is irrigated to fields within the

watershed at rates higher than crop uptake P accumulates in the soil. Unutilized P in animal excrement applied to crops and pastures and lagoon overflow are considered major sources of agricultural P that makes its way into streams and lakes of the watershed (Outlaw et al., 1995; Sweeten and Wolfe, 1993).

Phosphorus terms

Several terms are used to distinguish between different forms of P (Haygarth and Sharpley, 2000), but these terms often overlap. Algal-available P refers to the portion of P that is readily available to support algal growth (Haygarth and Sharpley, 2000). Some terms are derived based on processes used to measure them such as the filtration procedure used to differentiate between soluble P (SP) and particulate P (PP) (Haygarth and Sharpley, 2000). Inorganic P, organic P, orthophosphate P, reactive P, unreactive P, and total P (TP) are derived using chemical methods.

Phosphorus transport

In dairy operations, animal excrements are typically washed from milking parlors and feedlots. The effluent is usually screened to remove large particles then held in a lagoon or series of lagoons until the wastewater can be applied to cropland and pastures (Sweeten and Wolfe, 1994). During storage, larger and heavier particles settle to the bottom of the lagoon(s), but wind, thermal currents, escaping gases, and introduction of fresh effluent provide enough mixing to limit the settling of fine particles. The majority of the P in lagoon water applied as irrigation is associated with these suspended solids (Johnston, 1984).

Land application of P with lagoon water is generally in excess of the P requirement for the crop (Daniel et al., 1994; Maguire et al. 2000). The continual land application of P-laden effluent in quantities greater than P uptake by plants in the Bosque River Watershed has resulted in P buildup at the soil surface, thus increasing the potential for P loss in runoff (Sharpley et al., 1996; Sims et al., 1998). Phosphorus loss with surface runoff occurs mostly with the loss of sediments containing bound P, but some is also lost with P dissolved in the water (Haygarth and Sharpley, 2000). Pietilainen and Rekolainen (1991) suggest that as much as 60-90% of the P transported from cultivated lands is associated with sediments and organic matter. Phosphorus pollution of streams begins when rain detaches soil surface particles and carries them and water-soluble P with runoff water. Consequently, P in runoff usually positively correlates to soil P (Sharpley et al., 1996). While many in-stream processes including biotic uptake and deposition of P occur (Edwards et al., 2000), the P is eventually transported with flowing water to water body outlets where it is slowly released and able to support plant and algal growth.

The Bosque River and its outlet, Lake Waco, presently contain algal blooms. Since P is most often the limiting nutrient for algal growth in freshwater systems, reducing eutrophication caused by algal growth in these water systems is dependant on controlling P inputs from runoff (Little, 1988; Sharpley et al., 1994; Withers and Jarvis, 1998). Once in lakes however, the P deposited in the lake sediments has the potential to recycle, thus becoming available for eutrophication (Jacoby et al., 1982). This potential for recycling makes reducing P inputs from agricultural sources prior to entering rivers and lakes crucial. If considerable levels of P could be removed from the dairy effluent prior to land application as irrigation, P

content in the soil could gradually decrease with plant uptake and removal, thus reducing P in eroded sediments and runoff waters.

Wastewater treatment

Dairy effluents are similar to domestic wastewater; therefore methods used for treatment of human wastes may be used for animal wastes. Using these methodologies may not be economically feasible for the dairy industry (Grimm, 1972). Physical, chemical, and biological processes are commonly combined to improve overall efficiency in sewerage treatment facilities.

Physical treatment generally refers to removal of P by removal of solids either by a machine or settling. Physical treatments should be highly effective in P removal from lagoon effluent because much of the P is associated with suspended solids. Physical treatments include filtration and evaporation (Cheremisinoff, 1994). Filtration, which combines physical and chemical treatment, involves passing the wastewater through a reactive porous media, often including activated carbon, where the inorganic and organic chemicals are absorbed on the media. The clarified wastewater can then be discharged to a water body, applied to land as irrigation, or reused to flush through the system again. Evaporation requires heating the liquid to remove water, thus concentrating the solids and dissolved salts into slurry. The slurry is then applied to land as a fertilizer, added to wood chips to make compost, or disposed of in a landfill. These latter two processes may not be economical to remove the P from lagoon effluents effectively.

Most wastewater treatment facilities, including many animal waste facilities, pass their effluent through a screen or solid separator prior to chemical or biological treatment. Storage

lagoons can also serve as a means of physical treatment by allowing solids to settle to the bottom of the lagoon where, at a later time, they may be removed by dredging. Effluents in these lagoons are also subjected to biological activity, thus treatments in storage lagoons are not exclusively physical processes.

The addition of polymers, metal salts, and lime (CaOH and CaO) are chemical treatments of wastewater, used to separate solids and to reduce P through precipitation (Bowker and Stensel, 1990; Cheremisinoff, 1993). The metal salts of aluminum (Al) and iron (Fe) react with the phosphates in the solution and form metal-phosphate precipitates. The optimal pH for reduced P concentrations in wastewater with aluminum sulfate is 5.5 while the optimum dosage is 85 mg L^{-1} (Shindala and Bond, 1978). Aluminum is considered to be a secondary contaminant at 0.05-0.2 mg L^{-1}, and using Al salts may result in increased Al in the product water (Droste, 1997). For iron salts, the optimum wastewater pH is 4.8, and the dosage is 125 mg L^{-1} (Shindala and Bond, 1978). Iron salts are more expensive than aluminum sulfate, require a lower pH, and require a higher dosage. Disadvantages of using these metal salts include the production of noxious sludge, increased sludge production, and increased Fe and Al concentrations in the processed effluent. An advantage to using Fe salts is that biosolids, treated with ferric chloride, may be able to increase the P sorption capacity of a soil by increasing the Fe content (Penn and Sims, 2002).

Calcium (Ca) in lime (CaO and CaOH) reacts with phosphates to form calcium phosphates. The optimal wastewater pH for chemical precipitation of calcium phosphates with lime is 11.5, while the optimal dosage is about 1 g L^{-1} (Shindala and Bond, 1978). The difference between lime and the Al and Fe salts is that lime will alter the pH without needing other sources of pH adjustment, but there are problems with lime use because of difficulty in

handling the lime and difficulty in equipment maintenance. Lime also produces more sludge than other treatment processes, because a higher dosage is required. Chemical additions during wastewater treatment cause the P in biosolids to be less soluble and less available to plants (Kirkham, 1982; McCoy et al., 1986; Frossard et al., 1996). Sludges treated with Ca in the form of lime can supply P more efficiently to plants than Al- and Fe-precipitated biosolids (Soon et al., 1978).

Cationic polymers can be used to remove solids by promoting flocculation and increased sedimentation rates in wastewaters but are also more expensive than Al and Fe salts and lime (Letterman et al., 1999). Cationic polyacrylamides (PAM) have reduced total suspended solids in swine manure suspensions (Vanotti and Hunt, 1999). Polymers require lower optimal dosages (26-30 mg L^{-1}) than other forms of chemical treatment (Shindala and Bond, 1978). The optimal dosage depends on the polymer properties such as surface charge density as well as the surface properties of the solids (Mangraviter et al., 1978). Dao and Daniel (2002) found that cationic polymers combined with inorganic mineral treatments reduced dissolved reactive P and total suspended solids in manure suspensions.

The use of biological processes for wastewater treatment is well documented (Bowker and Stensel, 1990; Ramadori, 1987). In fact, 50 patents were processed from 1960 to 1993 that involved biological treatment of wastewater resulting in P removal (U.S. Environmental Protection Agency, 1993). Biological wastewater treatment processes can be divided into two main categories: fixed film and suspended growth (Drinan, 2001; Cheremisinoff, 1994). Fixed film systems involve microbial growth on and in the pores of a media. The microbial growth removes the organic wastes through oxidation as they are passed over the media. Suspended growth systems involve biomass that is mixed with the wastewater. Eventually the biomass is

removed from the system and land applied, composted, incinerated, or disposed of in a landfill (Rhyner et al., 1995). The most common example of suspended growth systems is the activated sludge process. The activated sludge process has been modified into several different processes. The Bardenpho process, AAO process, and University of Cape Town (UTC) process are some adaptations of the activated sludge processes (Smith and Scott, 2002). Each of these processes involves anaerobic, anoxic, and aerobic zones. The anaerobic zone accounts for the P removal as the microorganisms incorporate P into their biomass. The anoxic zone achieves denitrification, and the aerobic zone reduces the biological oxygen demand of the wastewater. Algal harvesting on lagoons and land application of effluent can also be considered biological removal of P. Although these methods can remove P efficiently, clarifiers may need to be added, equipment can be costly, and backup treatment machinery must be available in case of equipment failure (Bowker and Stensel, 1990). After biological treatment, plants may utilize the P from the biomass if the activated sludge is applied to land, but if landfilled the P would also be disposed along with the sludge. The cost, both financial and ecological, of sludge disposal greatly exceeds the costs of land application.

Land treatment is a common tool for reusing processed wastewater. It is also a means of treating unprocessed or under-processed wastewater. In slow rate systems (SR), plants and soil percolation act as the main treatment mechanisms (Droste, 1997; Rhyner et al., 1995). Using wastewater to irrigate fields is an example of a SR system. Rapid infiltration systems (RI) have higher hydraulic loading rate (Rhyner et al., 1995). Using soils with higher hydraulic conductivity and more pretreatment of the wastewater yields higher loading rates (Droste, 1997). The infiltration and permeability of these soils is high to very high which means that these soils are sandy. Overland flow (OF) is also an investigated form of land treatment. The

wastewater flows over a gradient covered in vegetation which uptakes nutrients into plants, slows the nutrients path downhill, and filters the wastewater (Droste, 1997). The soils for these systems have low permeability meaning that OF might be an ideal treatment in areas with clayey soils. There are several potential problems with treatments that utilize land application (Rhyner et al., 1995). Nutrients can accumulate in the soil, and these accumulated nutrients are exposed to erosion from wind and rain. Pathogens, if not reduced prior to land treatment, may become a nuisance. In systems where wastewater flows through the soil, soil pores can become clogged thus making the system less effective.

For financial reasons, dairies typically only use solid separation techniques and lagoons to reduce the P load in their effluent prior to irrigation (Grimm, 1972; Sweeten and Wolfe, 1993). Many dairies in the Bosque River watershed have purchased solid separators to remove solids from their effluent prior to entering the lagoon (Sweeten and Wolfe, 1993). Lagoons are constructed with the intention of solid removal. Occasionally, aluminum sulfate (alum) and lime are used to reduce P concentrations and to reduce the solids. Lime also can buffer the pH of the sludge produced.

Alternative methods for handling animal wastes

While lagoon storage and land application of manure or effluent are the most common methods of disposing of animal wastes, several other management options exist (Miner et al., 2000). A disadvantage of many of the alternatives for wastewater treatment is the failure to utilize the nutritional value of the wastewater.

Feed usually accounts for 50% or more of the cost of milk production (Johnson et al., 1991). Wastewater treatment resulting in potential food production could balance the costs of

wastewater treatment. Re-feeding manures to the livestock and poultry has proven to be successful, but public opinion and sanitation concerns prevent this alternative from being widely accepted in the dairy industry (Miner et al., 2000). Wilkie and Mulbry (2002) investigated the possibility of using benthic freshwater algae to recover the nutrients in dairy manure. Studies have shown that dairy cows fed a diet supplemented with a marine alga showed an increase in omega-3-fatty acid content which can potentially improve consumer health (Franklin et al., 1999).

Wetlands are a widely accepted wastewater treatment method that promotes biodiversity and generally involves little chemical additions (Cronk, 1996). The National Academy of Science (1992) defines biodiversity as the interactions among the variety and variability of living organisms, including genetic diversity, within the ecological complexes in which they occur. Both natural and constructed wetlands have proven effective in retaining and transforming nutrient inputs from municipal wastewater (Dierberg and Brezonik, 1983; Knight et al., 1987, Zhang et al., 2000). The interest in using constructed wetlands as an animal lagoon effluent treatment is fueled by the low-cost, low-technology, and low post-construction human maintenance (Hammer, 1992). The deposition of solids in wetlands decreases the levels of solids-related contaminants, such as P (Johntson et al., 1984). Pretreatment to reduce the suspended solids content of the wastewater, however, is essential for constructed wetlands to be effective (Reaves et al., 1994). Some downsides to using wetlands for wastewater treatment include that large areas of land are required, complexity of the system is not fully understood, there is a lack of precise design and operational criteria, pests may become problematic, and several growing seasons are needed to develop the system so that it operates at optimal levels (Rhyner et al., 1995).

The physical and chemical conversion of wastes to fuel is of increasing interest as the cost of energy grows. Animal manures have potential for biomass-to-energy conversion (Dagnell et al., 2000; Hoogwijk et al., 2003; Klauss, 1984). Eutrophic ponds can also serve as biomass for energy conversion (Klauss, 1984). From 100,000 cows, the accumulation of manure is nearly equal to the waste disposal of a large city (over 1 million people), but the drawback to using manure for energy is that manure must be dried prior to burning (Wender et al., 1974). Co-firing biomass with a base fuel has been successfully tested and demonstrated (Tillman, 2000).

Phosphorus recovery

While reduction of the soluble P concentrations before field application is necessary, finding methods that allow for economic removal is crucial for widespread adaptation of the technology. Compost and top-soil mixtures for nurseries, parks and recreational fields, home yards, and gardens are possible sinks for recovered solids from dairy effluent (Rhyner et al., 1995). Precipitation of soluble P remaining after removal of solids from dairy effluent might produce a fertilizer grade P compound that could be economically transported to remote fields. Precipitation of soluble P after solids are removed would produce a wastewater acceptable for continual land application to crops and pastures in a sustainable dairy system.

Although the nutrients in effluent have potential nutritional values to crops, P extracted as precipitates of Al or Fe are generally rendered unavailable for plant growth. Since natural P deposits are being depleted, recovering P from lagoon effluents and manures has been investigated (Gaterell et al., 2000; Driver et al., 1999; Stratful et al., 1999; Schuling and Andrade, 1999). Precipitation, sometimes referred to as crystallization, is a commonly

proposed step in methods of P recovery from wastewater (Angel, 1999; Greaves et al., 1999; Doyle and Parsons, 2002). Other treatment processes are also proposed in conjunction with crystallization such as biological P removal (Stratful et al., 1999). The Phostrip process is one known P precipitation systems combined with biological P removal. The Phostrip process is similar to most activated sludge processes; however, the sludge flows to an aerobic tank where P is released into the solution from the sludge (Smith and Scott, 2002). The sludge then returns to the aeration tank while the P rich supernatant is sent to another tank where lime is added to precipitate calcium phosphates. The precipitates are then removed from the tank. The Phosnix process removes phosphate from wastewater through the addition of magnesium hydroxide, which forms magnesium-ammonium phosphate, struvite (Smith and Scott, 2002).

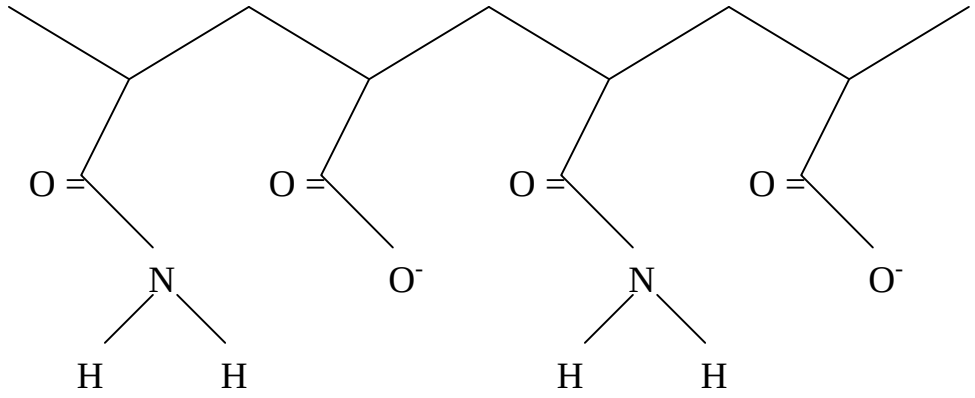
Principle treatment processes for wastewater reuse include flocculation during which suspended particles join and form aggregates that rapidly settle out of suspension or are of filterable size (Adin and Asano, 1998). Levine et al. (1985) estimated that flocculation processes could aggregate suspended solids with sizes ranging from 0.1 μm to 10 μm. Hamoda and Al-Awadi (1996) suggested that P concentrations in dairy effluent can be reduced using aluminum sulfate as a coagulant to reduce suspended solids. Using aluminum sulfate in systems that irrigate the effluent onto acid soils may result in reduced plant growth due to aluminum toxicity. The consequences of reduced plant growth are reduced uptake of P, reduced crop cover, and increased susceptibility of P runoff with surface erosion. Polymeric flocculants such as diallyl-dimethyl ammonium chloride (DADMAC) and polyacrylamide (PAM) (**Figure 1**) are widely used in the treatment of municipal wastewater. Use of polymeric flocculants eliminates many of the undesirable consequences associated with use of aluminum sulfate such as carry over of Al and the need for pH adjustments (Rout et al.,

1999). DADMAC is also widely used as an industrial flocculant. Cationic PAMs have been found to be more efficient than aluminum sulfate and to chemically react with dissolved organics to form colloids (Narkis and Rebhun, 1997). Narkis and Rebhun (1997) found that a certain form of cationic PAM reacted preferentially with organic matter in solutions.

If solids were removed from dairy effluent, an appreciable amount of dissolved organic and inorganic P would remain in the treated water. Phosphate chemistry (Song et al., 2002) suggests that raising the pH of the effluent would lead to precipitation of one or more calcium phosphate compounds. Angel (1999) precipitated amorphous calcium phosphate in sewage by raising the pH to 10 with magnesium oxide (MgO). After the magnesium oxide addition, the phosphates began to form around the magnesium oxide core (Angel, 1999). Calcium and phosphates have the potential to precipitate in multiple reactions (**Table 1**). While Mg is not incorporated into the calcium phosphate structure, some reports indicate that Mg can slow the rate of calcium phosphate formation (Nancollas, 1978). The Phostrip process is an example of a treatment that leads to calcium phosphate precipitation in wastewater treatment (Smith and Scott, 2002).

Struvite, a magnesium-ammonium phosphate, forms readily in human, swine, and poultry wastewater, and often causes problems with pipes and machinery (Yoon et al.,

a)



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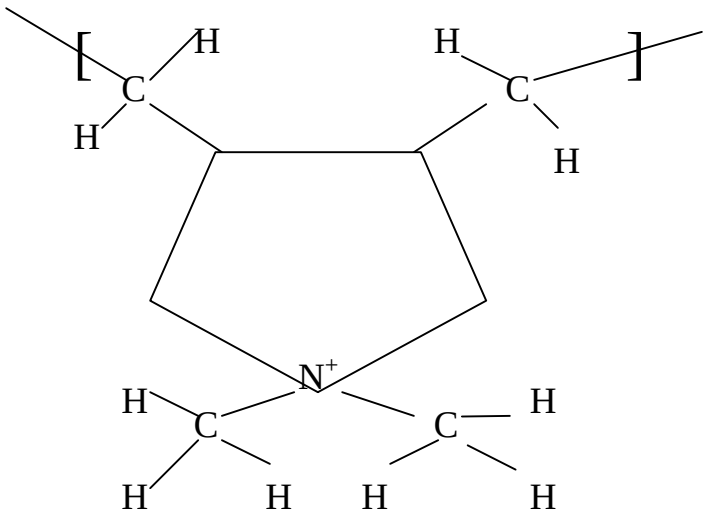


Figure 1: Basic chemical structures of PAM and poly-DADMAC. a) The chemical structure for polyacrylamide. b) The chemical structure of poly-DADMAC (Vorchheimer, 1981).

Table 1: Solubility constants of select calcium phosphates.

	Chemical Reaction	pK_s
1	$Ca_5OH(PO_4)_3$ (s) = 5 Ca^{2+} + 3 PO_4^{3-} + OH^-	-55.6
2	$Ca_5OH(PO_4)_3$ (s) = 2 {$Ca_2HPO_4(OH)_2$} surface + Ca^{2+} + HPO_4^{2-}	-8.5
3	{$Ca_2HPO_4(OH)_2$} surface = 2 Ca^{2+} + HPO_4^{2-} + 2 OH^-	-27
4	$CaHPO_4$ (s) = Ca^{2+} + HPO_4^{2-}	-7

Source: Stumm and Morgan, 1970

1999; Sievers, 1997; Buchanan et al., 1994). Anaerobic swine lagoon effluent contains struvite constituent ions (Mg^{2+}, NH_4^+, and PO_4^{3-}) thus reducing the need to add chemicals (Battistoni et al., 1997). Since nutrient values in dairy effluents are comparable to these other sources of wastes, struvite potentially could be formed in dairy wastewater. The Phosnix process, mentioned above, uses magnesium hydroxide to precipitate struvite. The critical pH for struvite precipitation is 7.6 (van Rensburg et al., 2003). The critical pH is the pH at which precipitation will begin. Nucleation is the controlling process for struvite formation because once it occurs the rate of crystal growth exceeds the rate of nucleation (Ohlinger et al., 1999; Gunn, 1976). Struvite precipitation has been used to remove P in several full- and pilot-scale waste treatment systems (Liberti et al., 1986; Ohlinger et al., 2000).

Schuling and Andrade (1999) recovered struvite from anaerobically digested calf manure. According to Taylor et al. (1963), the equilibrium reaction for struvite formation is:

Equation 1: $$MgNH_4PO_4 \cdot 6H_2O \leftrightarrow Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \qquad \text{pK=-13.2}$$

Ohlinger (1998) modeled struvite precipitation in wastewater to find minimum solubility between pH 10.3 and 10.7. A decrease in PO_4 and NH_4 concentrations due to struvite precipitation was observed as pH increased to 10.5 (Shin and Lee, 1997). Nelson et al. (2003) found minimum struvite solubility (maximum PO_4 removal) at pH 8.9 to 9.25. This range agrees with previous research done by Buchanan (1994) who suggested that minimum solubility occurred at pH 9.

Recovering the precipitate from the effluent might be problematic without a seeding agent or without additional filters. The mixing tank (**Figure 2**) on the dairy would be an ideal location for chemical additions because the mixer is already present and after mixing the

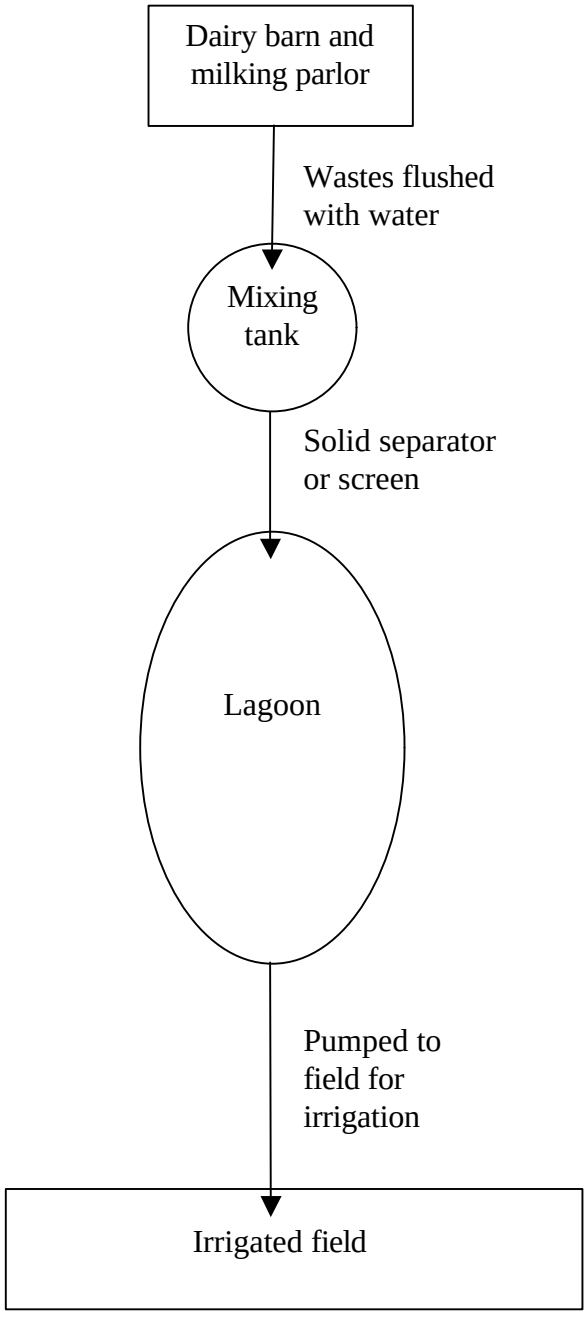


Figure 2: Flow schematic in dairy wastewater treatment.

effluent is pumped to a solid separator. The solid separator would remove the flocculated particles and precipitates from the effluent. Once the effluent enters the lagoon, further chemical treatments would be unfeasible for completely removing the P from the system.

Other benefits of flocculation and chemical treatment

Flocculants remaining in the effluent solution applied as irrigation water may also reduce erosion of P by improving aggregate stability at the soil surface and increase infiltration (Lentz et al., 1992; Lentz and Sojka, 1994; Sojka et al., 1998). Additionally, the use of polymers to induce flocculation has resulted in reduced pathogen levels in the wastewater (Cheremisinoff, 2002; Entry and Sojka, 2000). It is possible that the pathogens are bound to the organic solids that are removed by the flocculant. Polymer-treated manures remain stable in soils, and the release of dissolved reactive P from these manures is reduced compared to non-treated manures (Dao and Daniel, 2002). If solids were kept out of lagoons by a fast-acting flocculation process, the time between necessary dredging of solids from the lagoon could be extended.

Additionally, recent studies indicate that the majority of the solids that enter lagoons are converted to methane, a greenhouse gas, by microbes and lost to the atmosphere (Hamm, 2003, personal communication). Adler (1994) estimates that 2.3 million metric tons of methane are produced by animal production each year with 61% of that total originating from anaerobic lagoons. Methane emissions from lagoons are related to wind speed, lagoon water and air temperature, and the volatile solid load entering the system (Sharpe et al., 2002).

Research objectives

The overall goal of this research was to study practical means of reducing the P content of dairy effluent before it is applied to crops and pastures. As most of the P in dairy effluent is associated with suspended solids, the first objective was to compare methods of removing suspended solids. Traditional settling, as would occur in a lagoon, was compared to enhanced removal by flocculation. The second objective was to determine if P remaining in solution after the concentration of suspended solids were reduced could be removed through a chemical reaction that led to precipitation.

CHAPTER III

MATERIALS AND METHODS

Materials

Fresh samples of dairy effluent were obtained from a mixing tank (**Figure 2**) prior to solid separation and prior to entering the retention lagoon of a 2000-cow dairy in Comanche, Texas. The mixing tank was designed to collect and mix effluent streams and to pump the resulting material to a screening device to separate large solid particles before the effluent is stored in a lagoon. The samples were taken while the mixing pump was operating, so all solids in the effluent stream were suspended. Samples were collected in 200 L plastic drums, transported to Texas A&M University, College Station, and stored at room temperature (25^{o}C) in a research laboratory. The drums were vented daily to prevent pressure build up from gases. When placed in the laboratory, the drums were mixed to resuspended the solids in the effluent. The effluent was then allowed to settle with time.

Studies were conducted to: 1) determine the effect of solid settling on the elemental composition of the effluent, 2) determine the effect of removing suspended solids by flocculation on the elemental composition of the effluent, 3) compare the properties of untreated and flocculated solids, 4) determine if phosphates from the post-flocculated effluent could be separated by precipitation, and 5) characterize the precipitates if formed. These five studies are hereafter referred to as *Study 1* through *Study 5*.

Study 1 – Effect of settling

Subsamples were drawn in triplicate from a depth 20 cm below the surface of the effluent in a barrel. Forty mL-subsamples were drawn at the time of resuspension (Day 1) and every 14th day for 75 days. The subsamples were placed in 50 mL pyrex test tubes and covered with Parafilm ^{TM} until analysis. These samples received no chemical treatment prior to elemental analysis. In *Study 2* and *Study 3* these samples were considered as the control or null treatment. Samples were stored at 4^{o} C in a refrigerator until being analyzed to minimize changes in the chemical composition of the effluent caused by microbial and thermodynamic reactions. Aliquots were taken from the test tubes and analyzed for extractable P, sodium (Na), total Kjeldahl nitrogen (TKN), calcium (Ca), magnesium (Mg), zinc (Zn), manganese (Mn), copper (Cu), iron (Fe), and potassium (K) concentrations.

Study 2 - Flocculation

A cationic polyacrylamide, PAM (H2-480Z-C), courtesy of Qemifloc (Qemi International, Houston, Texas) was mixed with diallyl-dimethyl ammonium chloride (DADMAC), in a 1 to 4 (PAM:DADMAC) mass ratio. This ratio was chosen based on preliminary experiments, which suggested greatest flocculation at this ratio. Hereafter, the mixture will be referred to as the flocculant.

Similar to Study 1, 40 mL subsamples were drawn in triplicate from 20 cm below the effluent surface in the barrel and placed 50 mL test tubes. Flocculant was added to the 40 mL of effluent in a 50 mL test tube. After treatment, the test tube was covered with Parafilm^{TM} and inverted three times to mix the effluent and the flocculant. The flocculated particles were then allowed to settle overnight in the test tube. Treatment concentrations of flocculant in the

effluent were 0, 0.13, 0.42, 1.30, and 3.73 mg L^{-1}. While the first three treatment concentrations were chosen based on preliminary lab tests and multiples of 3 thereafter, the final flocculant concentration was chosen because as a multiple of 3 the treatment would be too syrupy to apply on a 1 mL basis. After mixing, the solution was allowed to settle, decanted, and analyzed for extractable P, Na, TKN, Ca, Mg, Zn, Mn, Cu, Fe, and K concentrations. Each treatment, including a control treatment, was replicated three times, and analyzed along with blanks and standards.

Study 3 – Properties of the separated solids

After 75 days, 380 L of the effluent stored in the barrels was re-suspended. One half of the re-suspended effluent was treated to produce a final flocculant concentration of 1.3 mg L^{-1}. The effluent was allowed to react with the flocculant for 48 hours and was then screened through a 2 mm mesh to collect the solids. After removal of the solids, the effluent was transferred into a clean barrel for later studies. Solids were dried in an oven at 60^{o}C in stainless steel pans. The remaining 190 L of resuspended effluent was allowed to resettle for a week then screened using the same mesh to remove the solids from the suspension. The effluent was allowed to settle to ease straining. The effluent, after solid removal, was collected and placed into a clean barrel for later use. The solids were dried at 60^{o}C. A food processor was used to break dried and caked solids from both treatments into smaller, more uniform pieces. The water holing capacity of the solids at -100 kPa, -33 kPa, and -10 kPa water potential was determined with a pressure plate apparatus (USDA, 1996). Knowledge of water holding capacity is important for two reasons. First, water-holding capacity is directly related to surface area, which is related to particle size; therefor comparing the water holding capacity

of solids increases smaller particle sizes. Knowing which approximate particle sizes were removed by the flocculant helps interpret the associations of certain nutrients with particle size fractions. Second, if the solids were marketed as a soil admendment, the effect of the compost on the surface soil moisture regime is important because it impacts the ability of the soil to supply water for plant growth. Subsamples of the solids were analyzed for extractable P, Na, TKN, Ca, Mg, Zn, Mn, Cu, Fe, and K concentrations.

Study 4 – Precipitation

The simplest P removal system would be to precipitate the soluble P immediately after flocculation of the solids, but before their removal. To test the potential for precipitation in such case, 40 mL subsamples of the effluent were drawn from 20 cm below the surface of the effluent stored in the barrels and placed in 50 mL test tubes. These subsamples were treated with flocculant to produce flocculant concentrations of 0, 0.13, 0.42, 1.3, and 3.73 mg L^{-1}. These samples were then covered with Parafilm^{TM} and mixed by overturning the test tube three times. The test tubes were allowed to settle for an hour before further treatment. Ammonium hydroxide (3 % NH_3 assay) was then added to the test tube to raise the pH of the effluent to near 9. Equilibrium equations indicate that calcium and magnesium-ammonium phosphates would precipitate at this pH (Buchanan et al., 1994; Doyle and Parsons, 2002; House, 1999; Nelson et al., 2003; Snoeyick and Jenkins, 1980; Song et al., 2002). After addition of ammonium hydroxide, the test tube was again covered, mixed by overturning three times, and then allowed to settle overnight. Following settling, the solution was decanted and analyzed for extractable P, Na, TKN, Ca, Mg, Zn, Mn, Cu, Fe, and K. Each treatment was replicated three times, and analyzed with blanks and standards.

Study 5 – Characterization of the precipitates

To collect enough precipitate for elemental analysis, a larger quantity of the effluent was required for precipitation. The effluents from which the solids were removed in *Study* 3 were used to collect precipitates. Since the flocculated effluent had most of the suspended solids removed, 20 L of the untreated effluent were centrifuged at 4472 g-force to remove suspended solids. After centrifugation the samples were decanted into a clean plastic bucket. Five hundred mL of effluent with solids removed was poured into an Erlenmeyer flask. The pH was measured using a pH electrode. The initial pH's of the effluents after removal of solids were 8.2. Our target pH's were 8.6, 8.9, and 9.4. To produce pH 8.6, 0.5 mL of NH_4OH solution (30% NH_3) was added to the untreated solution. To reach pH 8.9, another 0.5 mL, a total of 1 mL, was added; and an additional 2 mL, a total of 3 mL, was required to increase the pH to 9.4. Each of these treatments, including a control, was replicated three times for both the flocculated and untreated effluent. After addition of the NH_4OH solution, the samples were mixed using a Thermolyne Nuova II stirrer and allowed to settle overnight. The solutions were then decanted into test tubes and submitted for P, Na, TKN, Ca, Mg, Zn, Mn, Cu, Fe, and K analysis. The precipitates formed were poured into smaller jars, and dried with approximately 45 mL of effluent solution at a temperature of 55^{o} C. A 45 mL sample of the effluent solution without the precipitate was dried to account for salts precipitation upon drying. After drying these precipitates were scraped from the bottom of the jars and ground using a mortar and pestle. Once ground, samples were placed back into the jars and covered until they could be analyzed by X-ray diffraction (XRD) and for analysis of extractable P, Na, TKN, Ca, Mg, Zn, Mn, Cu, Fe, and K concentrations.

Sample analysis

The Texas Cooperative Extension Soil, Forage and Water Testing Lab analyzed samples for P and N concentrations and major cationic composition. Concentration of cations extractable Fe, Zn, Mn, and Cu were also measured to document any accumulations of these elements in the effluent. The pH of the effluent was measured using an Orion pH/ISE meter (Model 710A). Samples were digested using adding salt-catalyst-sulfuric acid and an aluminum block to heat the mixture to its boiling point (Nelson and Sommers, 1973; Nelson and Sommers, 1980; Parkinson and Allen, 1975). From this mixture, N was determined colorimetrically, and other nutrients were determined by inductively coupled plasma (ICP). The laboratory results were used to compare P removal with the amount of flocculant used, the pH of the effluent, time allowed for the effluent to settle, and removal of specific cations.

Identification of the minerals in the precipitate was made by analysis of ions removed from solution and by X-ray diffraction (XRD) using a CuKα radiation (154.19 pm). The XRD technique illuminates a powdered sample in a holder with x-rays of a fixed wave-length; the intensity of the reflected radiation is recorded using a goniometer (Joint Committee on Powder Diffraction Standards, 1974). The reflection angle is used with the data to calculate inter-atomic spacing or D-spacing of mineral crystals. The D-spaces with the highest intensities in the pattern of a precipitate sample were compared to peaks of known minerals listed in reference manuals (Joint Committee on Powder Diffraction Standards, 1974).

CHAPTER IV

RESULTS

The results showing reduction of P, N, Ca, and Mg concentrations in treated dairy effluent will be displayed graphically for all studies. The graphs for other nutrients and numerical data are in Appendices A through E. The error bars for the graphs represent 95% confidence intervals. All results reported to be significant are with 95% confidence (α =0.05) unless otherwise stated.

Study 1 – Effect of settling

Removal of suspended solids by settling alone reduced P concentration to about 1/4 of its original value (**Figure 3**). Decrease in N concentration with removal of the solids by settling was negligible (**Figure 3**). Concentrations of Ca and Mg decreased to about 3/4 of their initial values (**Figure 4**). The decreases in Mn were similar those of Ca and Mg. Concentrations of all other micronutrients decreased with time, but not to the extent of Ca, Mg, and Mn (**Table 2**).

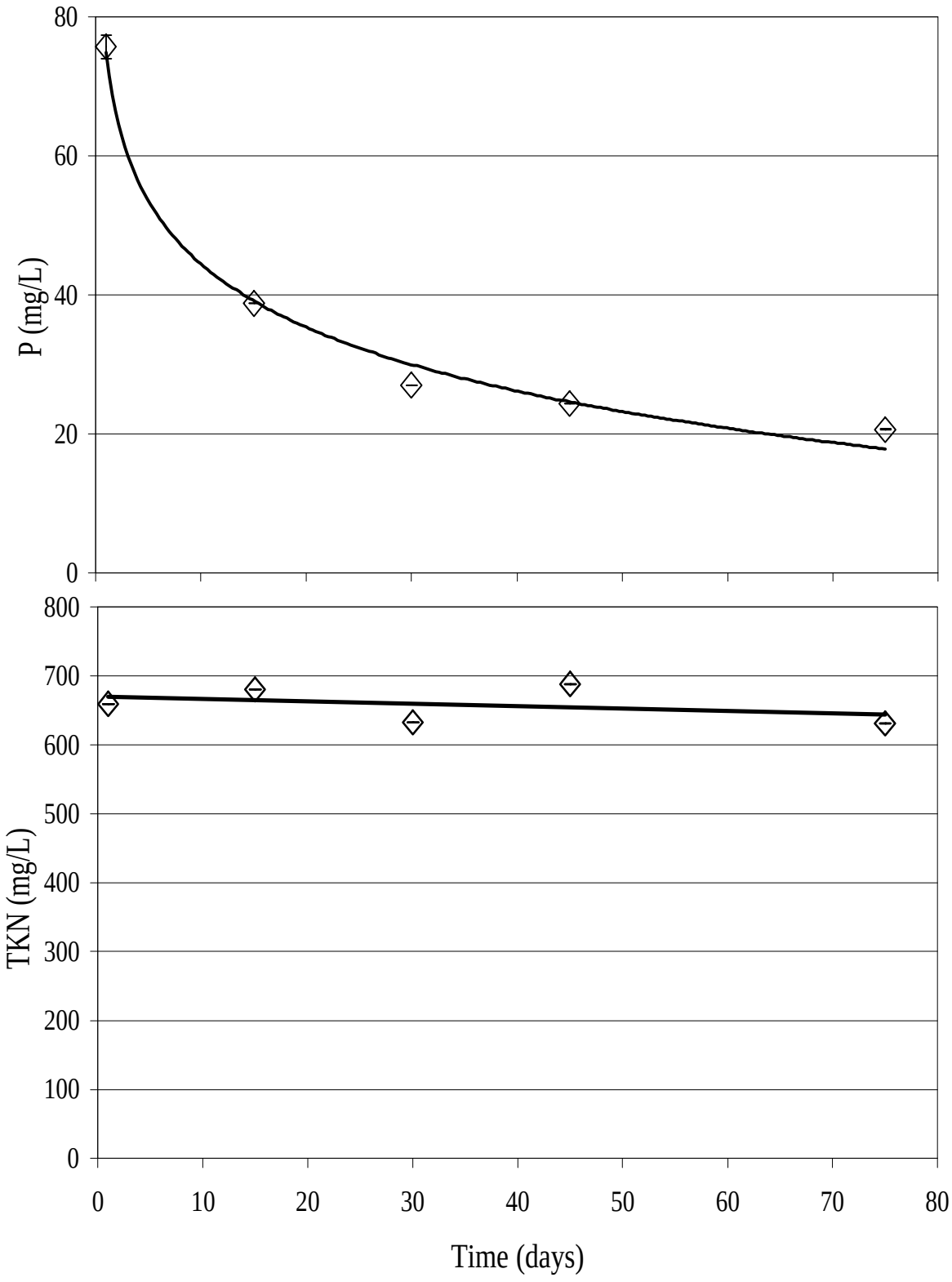


Figure 3 – Changes in P and N concentrations with settling time.

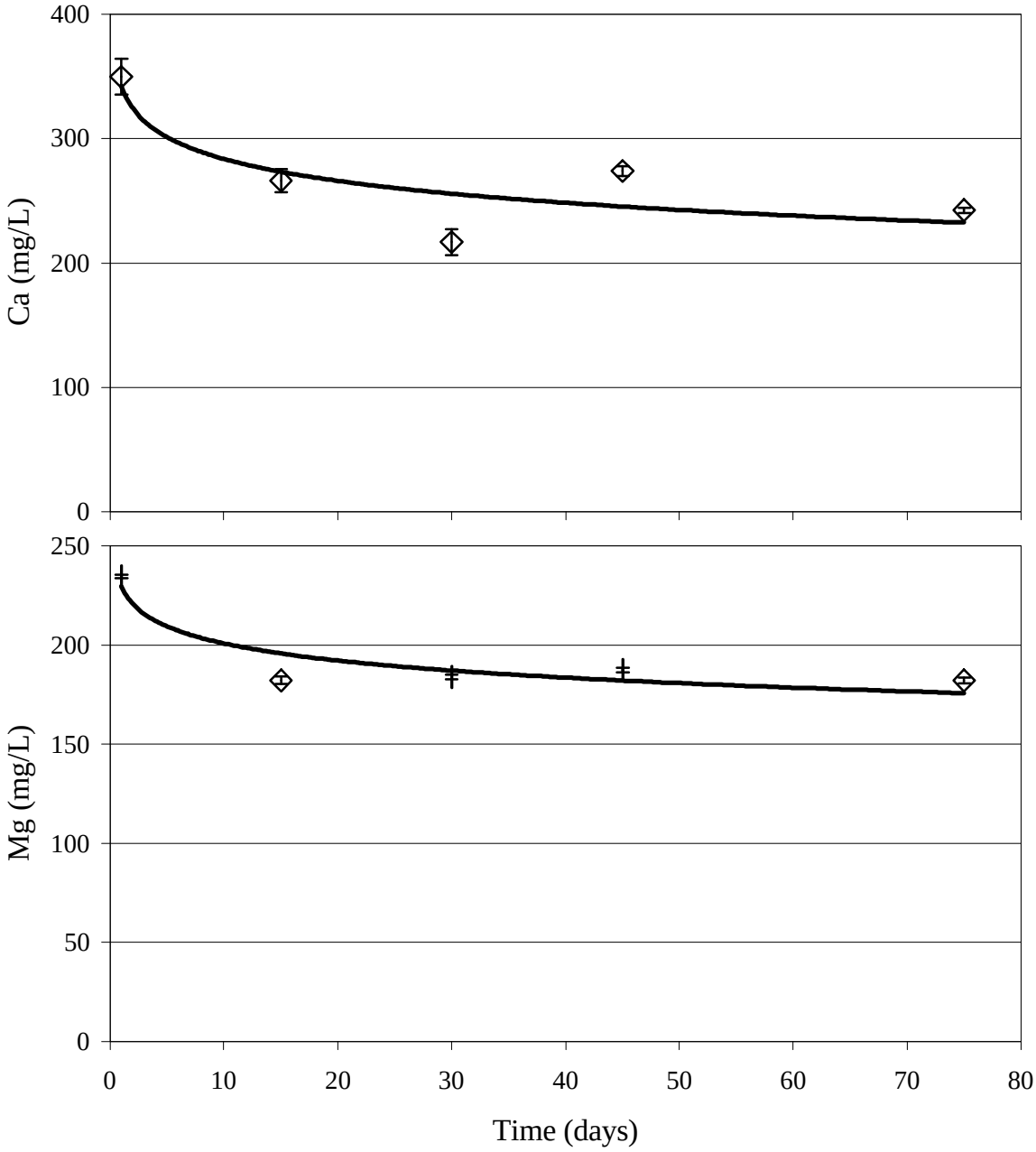


Figure 4: Ca and Mg concentrations with settling time.

Table 2: Average Cu, Fe, K, Mn, Na, and Zn concentrations (mg L^{-1}) and percent change in the effluent with time. All confidence intervals are for $\alpha = 0.05$. Corresponding figures can be found in the Appendix A- Effect of settling.

Element	Day 1	Day 15	Day 30	Day 45	Day 75
	mg L^{-1} (% change)	mg L^{-1} (% change)	mg L^{-1} (% change)	mg L^{-1} (% change)	mg L^{-1} (% change)
Cu	0.505 ± 0.010 (0)	0.305 ± 0.007 (-40)	0.437 ± 0.008 (-13)	0.270 ± 0.001 (-47)	0.271 ± 0.027 (-46)
Fe	8.910 ± 0.838 (0)	3.333 ± 0.577 (-63)	3.717 ± 0.154 (-58)	3.567 ± 0.172 (-60)	5.755 ± 0.849 (-35)
K	1157 ± 11 (0)	1045 ± 11 (-10)	1026 ± 6 (-11)	1093 ± 8 (-6)	1064 ± 8 (-8)
Mn	1.475 ± 0.218 (0)	0.696 ± 0.239 (-53)	0.511 ± 0.015 (-65)	0.487 ± 0.003 (-67)	0.411 ± 0.004 (-72)
Na	358.3 ± 7.1 (0)	298.7 ± 3.6 (-17)	310.3 ± 2.8 (-13)	305.9 ± 3.3 (-15)	277.5 ± 9.8 (-23)
Zn	1.923 ± 0.087 (0)	1.484 ± 0.094 (-23)	0.769 ± 0.048 (-60)	0.831 ± 0.005 (-57)	0.854 ± 0.068 (-56)

Study 2 – Flocculation

The DADMAC/PAM treatment resulted in rapid flocculation. After formation, the floc either floated to the top or sank to the bottom, depending on the amount of air trapped within the floc. Addition of flocculant quickly reduced concentrations of nutrients (**Figure 5, Figure 6, Table 3)**. It was apparent that flocculant was most efficient in reducing concentrations before the larger solids had time to settle. Flocculation accomplished a reduction in P concentration in one day comparable to that achieved after 30 days of settling.

Study 3 – Properties of the solids

The amount of solid mass recovered from the flocculated versus the untreated effluent indicated that the flocculant removed a considerably greater mass of the total solids from the effluent. From the 190 L of wastewater treated with 0.13 mg L^{-1} of flocculant, 834 grams of dry solids were recovered. The mass of flocculant added was 0.246 g. Based on the total mass of the flocculated solids recovered the mass of the flocculant was negligible. Straining only recovered 585 grams dry solids. By subtracting the dry mass of the untreated solids from the dry mass recovered by flocculated treatment, one can estimate the amount of solid material removed by the flocculant that would have otherwise remained in the effluent. Flocculation removed twice as much solids on a mass basis as straining alone. In addition to greater recovery of solids, the flocculated solids held about 0.3 kg/kg more water than the untreated solids at -10, -33, and -100 kPa of water potential (**Figure 7**). All tested nutrients were removed in greater quantities by flocculation than with no treatment (**Figure 8**). Phosphorus, the element targeted, was removed in large quantities by both treatments, but flocculation removed 20% more P.

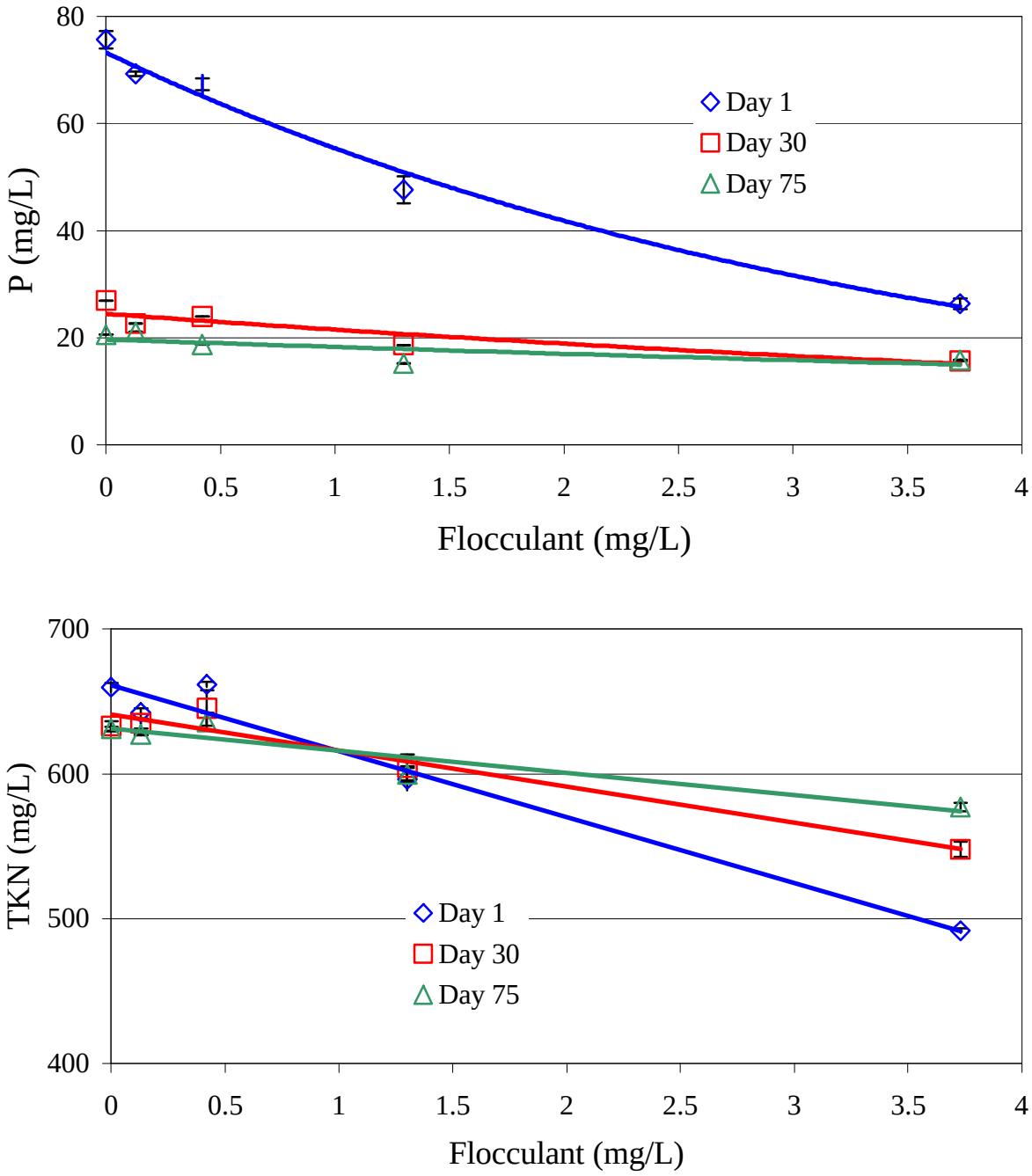


Figure 5: Changes in P and N (mg L^{-1}) with flocculant concentrations.

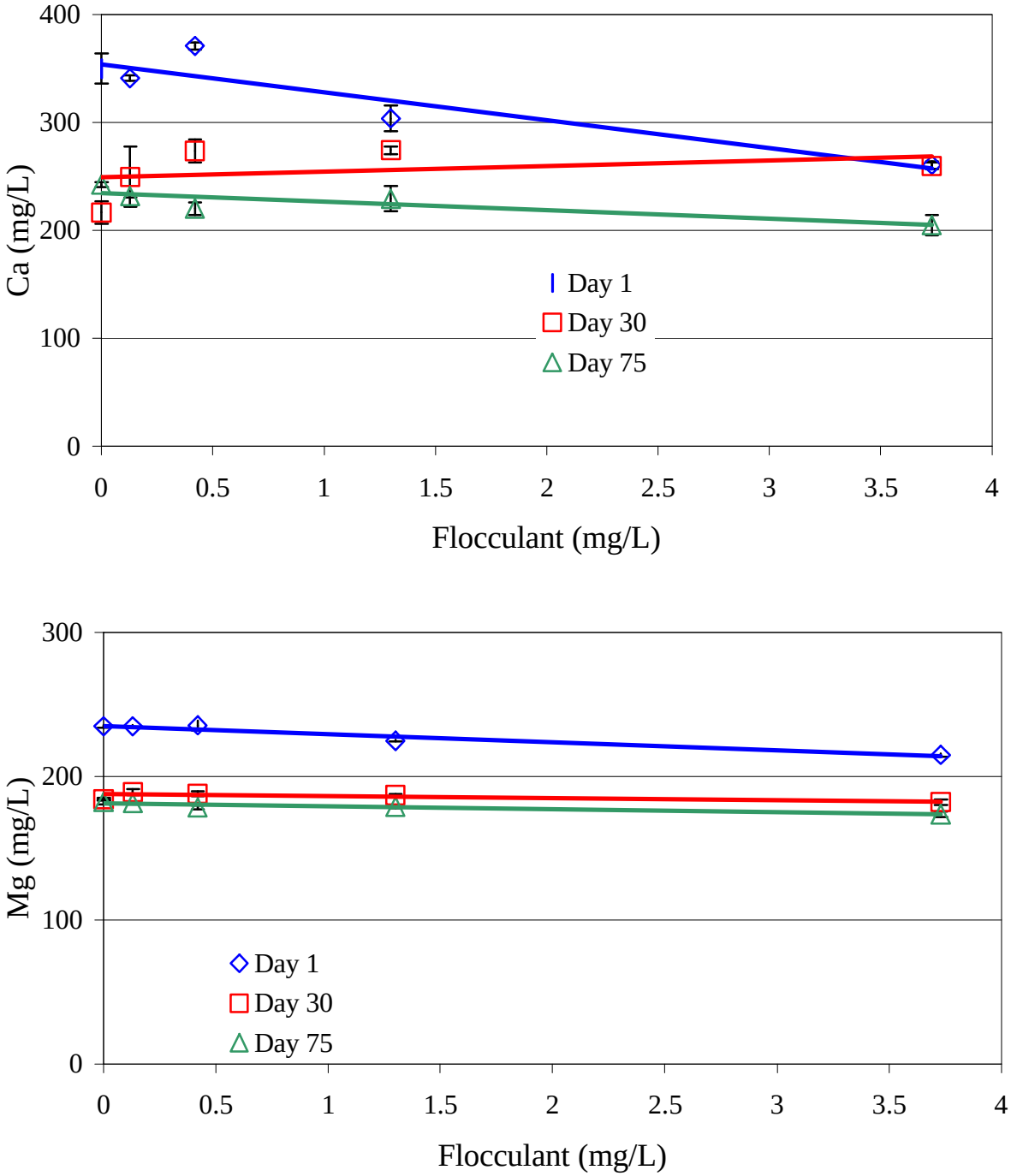


Figure 6: Changes in Ca and Mg (mg L^{-1}) with flocculant concentration.

Table 3: Average Cu, Fe, K, Mn, Na, and Zn (mg L^{-1}) and percent change with increasing flocculant concentration over days 1, 30, and 75. All confidence intervals are for $\alpha = 0.05$. Corresponding graphs can be found in Appendix B – Flocculation.

Element	Day	Flocculation Treatment mg L^{-1} (% change from day 1)			
		0	0.13	1.30	3.73
Cu	1	0.505 ± 0.011 (0)	0.456 ± 0.005 (-10)	0.285 ± 0.016 (-44)	0.055 ± 0.009 (-89)
	30	0.437 ± 0.008 (-13)	0.293 ± 0.003 (-42)	0.411 ± 0.096 (-19)	0.072 ± 0.03 (-86)
	75	0.271 ± 0.027 (-46)	0.374 ± 0.007 (-26)	0.265 ± 0.040 (-48)	0.122 ± 0.001 (-76)
Fe	1	8.910 ± 3.470 (0)	6.680 ± 2.601 (-25)	4.683 ± 1.824 (-51)	1.513 ± 0.589 (-83)
	30	3.717 ± 1.447 (-58)	3.327 ± 1.275 (-63)	1.873 ± 0.730 (-79)	1.140 ± 0.444 (-87)
	75	5.755 ± 2.241 (-35)	5.688 ± 2.215 (-36)	6.833 ± 2.661 (-23)	5.746 ± 2.238 (-36)
K	1	1157 ± 11 (0)	1157 ± 4 (0)	1147 ± 2 (-1)	1093 ± 3 (-6)
	30	1026 ± 6 (-11)	1051 ± 3 (-9)	1054 ± 2 (-9)	1007 ± 7 (-13)
	75	1065 ± 8 (-8)	1070 ± 3 (-8)	1076 ± 4 (-7)	1019 ± 6 (-12)
Mn	1	1.475 ± 0.218 (0)	1.100 ± 0.016 (-25)	0.794 ± 0.048 (-46)	0.354 ± 0.006 (-76)
	30	0.511 ± 0.015 (-65)	0.546 ± 0.032 (-63)	0.380 ± 0.003 (-74)	0.283 ± 0.006 (-81)
	75	0.411 ± 0.004 (-72)	0.414 ± 0.006 (-72)	0.368 ± 0.033 (-75)	0.286 ± 0.010 (-81)
Na	1	385 ± 7 (0)	367 ± 1 (-5)	368 ± 3 (-4)	355 ± 1 (-8)
	30	310 ± 3 (-19)	315 ± 1 (-18)	319 ± 2 (-17)	309 ± 2 (-20)
	75	278 ± 10 (-28)	299 ± 1 (-22)	299 ± 1 (-22)	283 ± 3 (-26)
Zn	1	1.923 ± 0.088 (0)	1.693 ± 0.018 (-12)	0.980 ± 0.068 (-49)	0.117 ± 0.023 (-94)
	30	0.769 ± 0.048 (-60)	0.892 ± 0.009 (-54)	0.603 ± 0.161 (-69)	0.064 ± 0.005 (-97)
	75	0.854 ± 0.068 (-56)	0.935 ± 0.124 (-51)	0.706 ± 0.138 (-63)	0.070 ± 0.006 (-96)

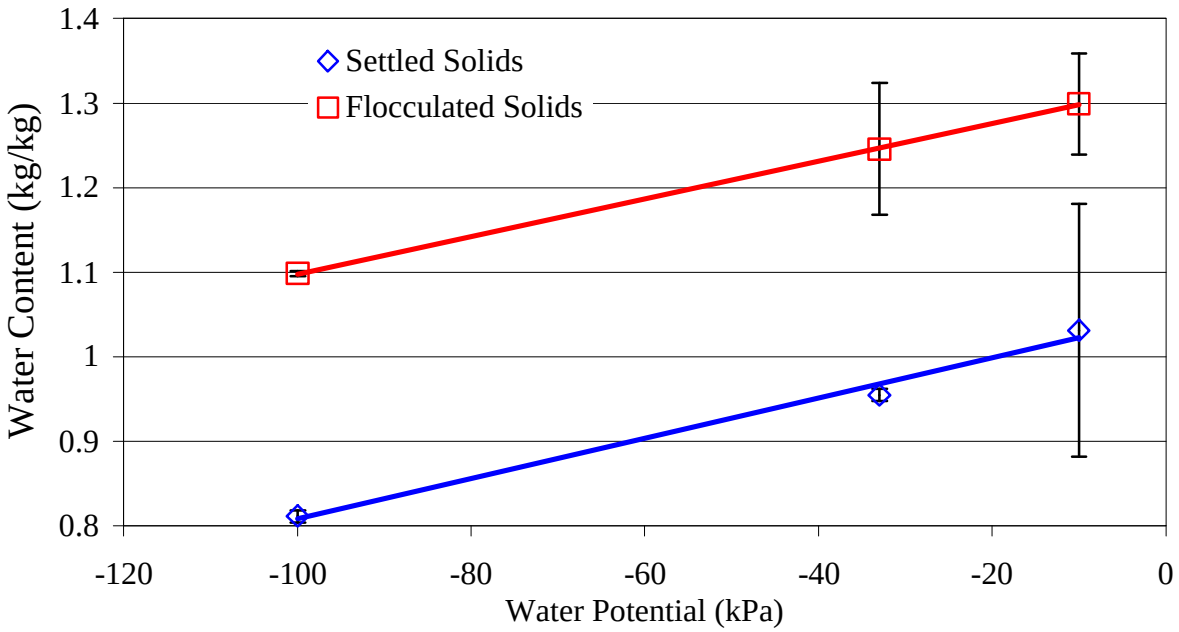


Figure 7: Water holding capacity of the untreated and flocculated solids.

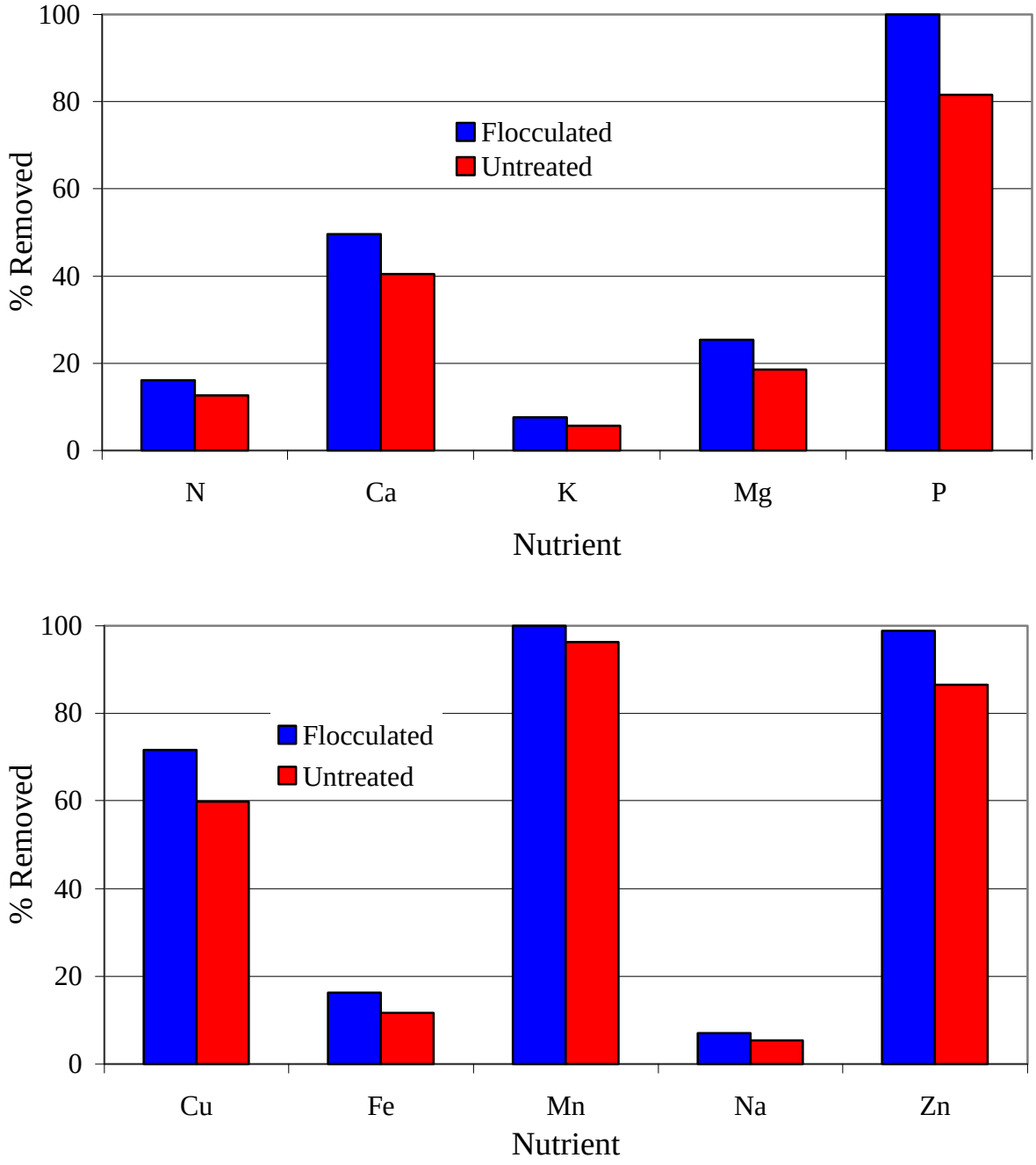


Figure 8: Percentages of N, Ca, K, Mg, P, Cu, Fe, Mn, Na and Zn removed from the original effluent by untreated settling and by flocculation.

Study 4 – Precipitation

After ammonium hydroxide was added to the effluent from which the solids had been removed by flocculation and screening, the solution immediately became cloudy, indicating that a precipitate was forming. After the test tube was allowed to settle overnight, the flocs in the test tubes treated with ammonium hydroxide were often layered with lighter colored streaks. These streaks may have been the precipitate bound to the flocs.

In all flocculant treatments on Day 45, P decreased as the pH increased (**Figure 9**). At the highest level of flocculant and highest pH, P concentration decreased about 90%. Total N increased with increased pH, but this increase in N was expected since ammonium hydroxide was added to raise the pH. In *Study* 5, the actual increases in TKN are compared to those expected had the N in the ammonium hydroxide completely remained in solution. Other tested elements also decreased with pH except for K and Na concentrations (**Figure 10, Table 4).** On a mmol L^{-1} basis, Ca and P concentrations follow a close relationship as pH and flocculant concentrations increase (**Figure 11**). Magnesium and P concentrations on a mmol L^{-1} basis also decrease over flocculant concentration and pH.

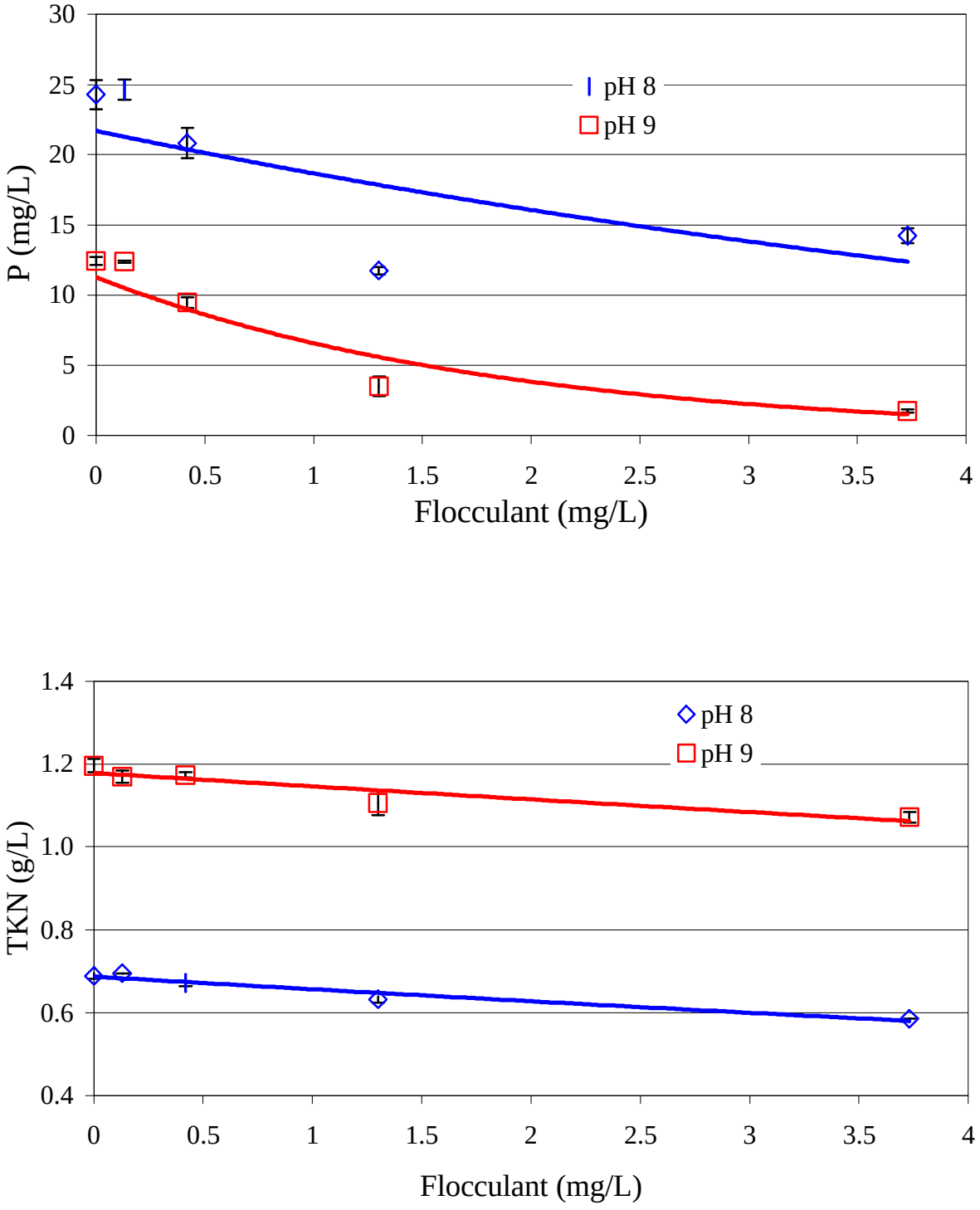
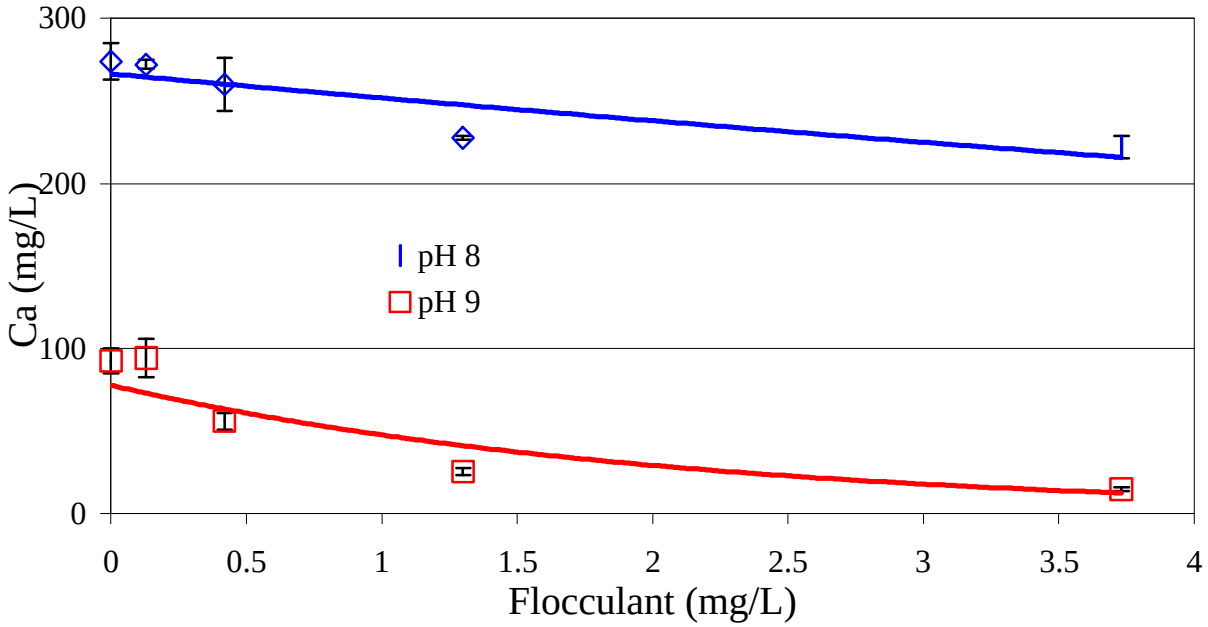


Figure 9: Changes in P and TKN concentrations in the effluent with pH on Day 45.



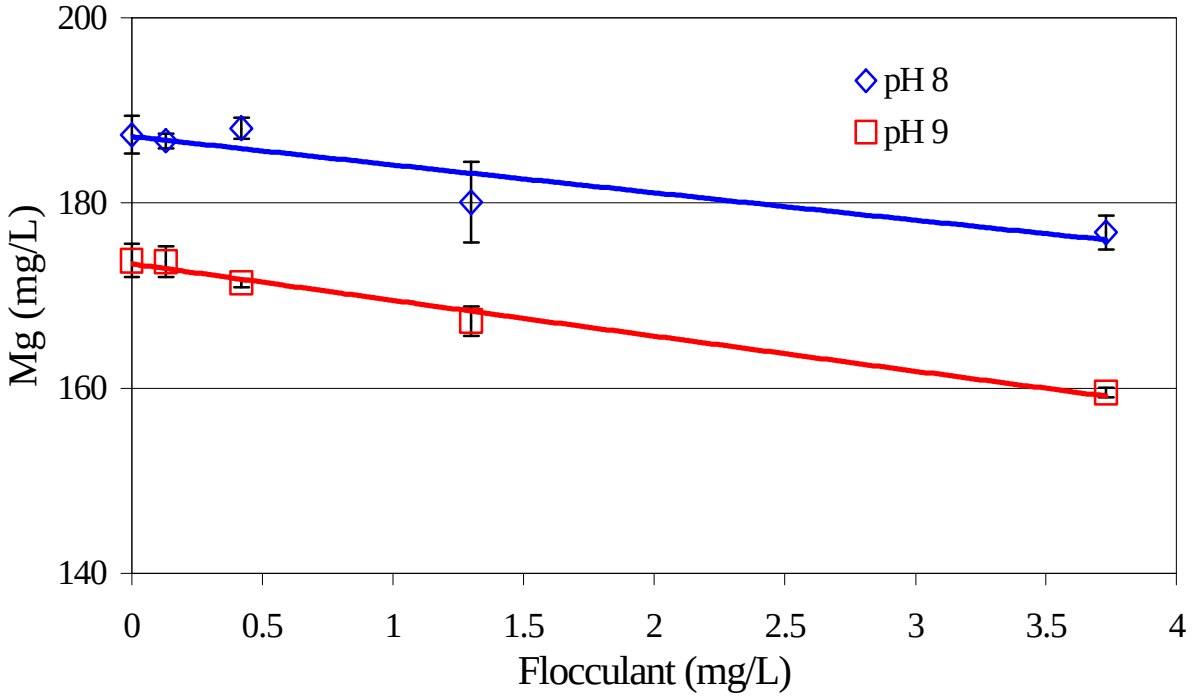


Figure 10: Changes in Ca and Mg concentrations in the effluent with pH on Day 45.

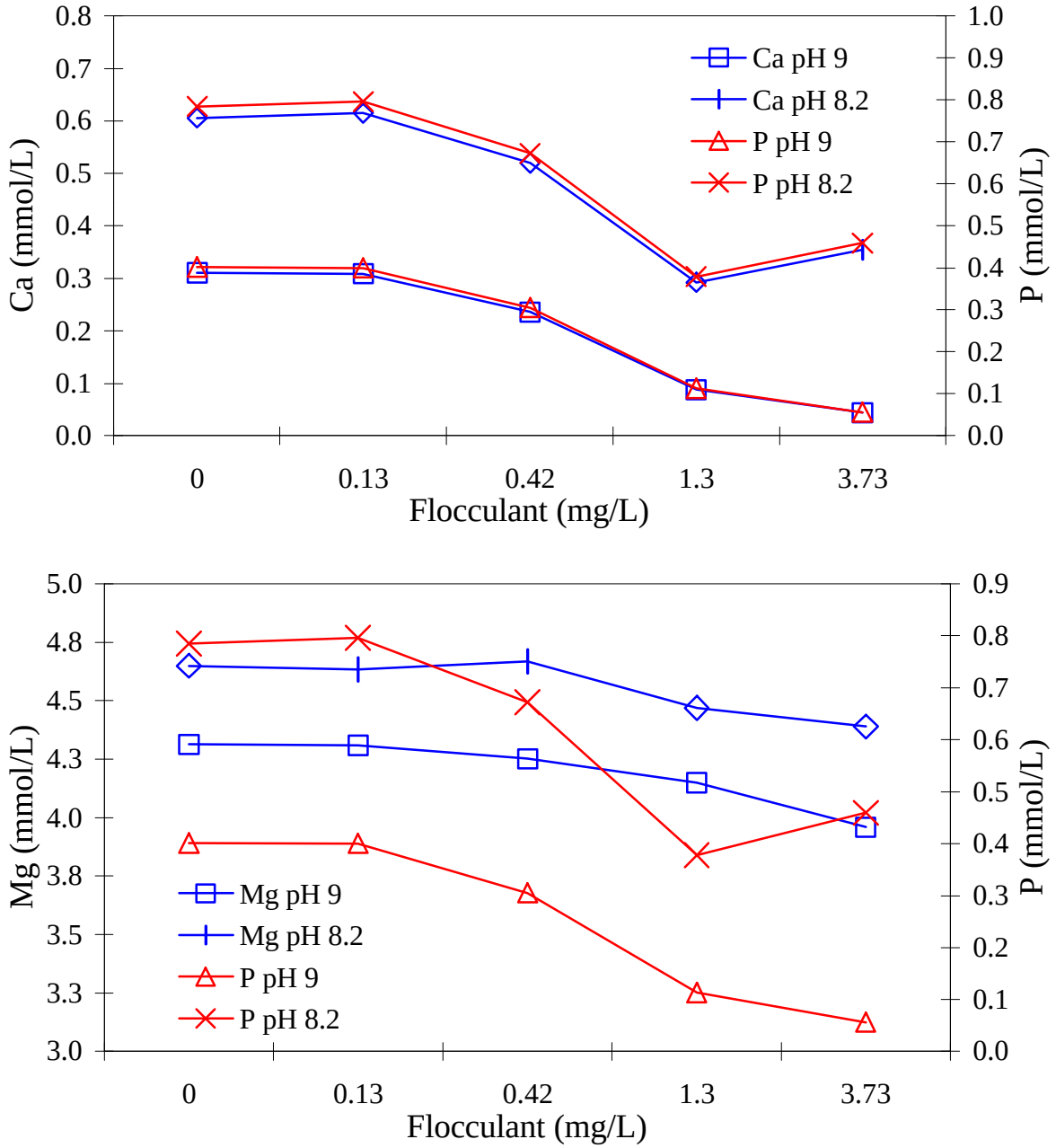


Figure 11: Changes in Ca, P, and Mg concentrations (mmol L^{-1}) in the effluent over flocculant concentrations as the pH is increased from 8.2 to 9 on Day 45.

Table 4: Changes in the average Cu, Fe, K, Mg, Mn, Na, and Zn concentrations and percent change in the effluent as the pH is raised on day 45. All confidence intervals are for $\alpha = 0.05$. Corresponding graphs can be found in Appendix D – Precipitation with flocculation.

Element	Flocculant	pH = 8	pH = 9
	mg L^{-1}	mg L^{-1} (% change)	mg L^{-1} (% change)
Cu	0	0.270 ± 0.004 (0)	0.270 ± 0.008 (0)
	0.13	0.267 ± 0.016 (-1)	0.280 ± 0.005 (+4)
	0.42	0.206 ± 0.000 (-24)	0.195 ± 0.021 (-28)
	1.30	0.066 ± 0.004 (-98)	0.067 ± 0.016 (-98)
	3.73	0.024 ± 0.002 (-99)	0.026 ± 0.007 (-99)
Fe	0	3.567 ± 0.458 (0)	3.089 ± 0.333 (-13)
	0.13	3.216 ± 0.170 (-10)	2.902 ± 0.053 (-19)
	0.42	2.432 ± 0.132 (-32)	2.118 ± 0.076 (-41)
	1.30	1.752 ± 1.240 (-51)	5.560 ± 2.606 (+55)
	3.73	1.232 ± 0.129 (-65)	0.620 ± 0.207 (-83)
K	0	1094 ± 10 (0)	1090 ± 11 (0)
	0.13	1093 ± 2 (0)	1086 ± 5 (-1)
	0.42	1106 ± 2 (+1)	1078 ± 5 (-1)
	1.30	1089 ± 12 (0)	1064 ± 1 (-3)
	3.73	1037 ± 6 (-5)	1024 ± 2 (-6)
Mn	0	0.487 ± 0.004 (0)	0.374 ± 0.009 (-23)

Table 4: Continued

Element	Flocculant	pH = 8	pH = 9
Mn	0.13	0.476 ± 0.008 (-2)	0.376 ± 0.009 (-23)
	0.42	0.414 ± 0.008 (-13)	0.289 ± 0.011 (-41)
	1.30	0.359 ± 0.191 (-26)	0.229 ± 0.026 (-53)
	3.73	0.213 ± 0.002 (-56)	0.127 ± 0.018 (-74)
Na	0	305.9 ± 3.6 (0)	307.7 ± 3.0 (+2)
	0.13	311.7 ± 2.0 (+3)	309.4 ± 3.5 (+2)
	0.42	314.3 ± 2.6 (+4)	305.3 ± 1.5 (+1)
	1.30	306.4 ± 4.9 (+1)	299.7 ± 1.0 (-1)
	3.73	298.1 ± 5.4 (-2)	290.3 ± 1.9 (-4)
Zn	0	0.831 ± 0.011 (0)	0.782 ± 0.026 (-6)
	0.13	0.786 ± 0.025 (-5)	0.745 ± 0.006 (-10)
	0.42	0.620 ± 0.009 (-25)	0.544 ± 0.058 (-35)
	1.30	0.221 ± 0.021 (-73)	0.207 ± 0.018 (-75)
	3.73	0.081 ± 0.011 (-90)	0.059 ± 0.004 (-93)

Study 5 – Characterization of the precipitates

For both the untreated and flocculated effluents, the P content in the solutions decreased as the pH increased (**Figure 12**). The concentration of P in the precipitate increased directly with the pH of the effluent. Total N concentrations in the solution conversely increased directly with pH due to addition of N as ammonium hydroxide (**Figure 13, Figure 14**). The reactions of Ca, Mg, K, and the other micronutrients varied (**Figure 15, Figure 16, Table 5, Table 6)**.

X-ray diffraction patterns indicate little differences between the precipitates of the flocculated and untreated effluents (**Figure 17)**. Comparisons of the D-spaces where the peaks occurred with D-spaces of peaks for known minerals were made using a mineral reference book. These comparison suggest that monohydrocalcite ($CaCO_3*H_2O$), calcium phosphate ($Ca_3(PO_4)_2$), sylvite (KCl), halite (NaCl), and some struvite ($MgNH_4PO_4*6H_2O$) are present in the precipitates. The pattern from the dried effluent sample indicated the presence of sylvite, calcium phosphate, halite, and monohydrocalcite.

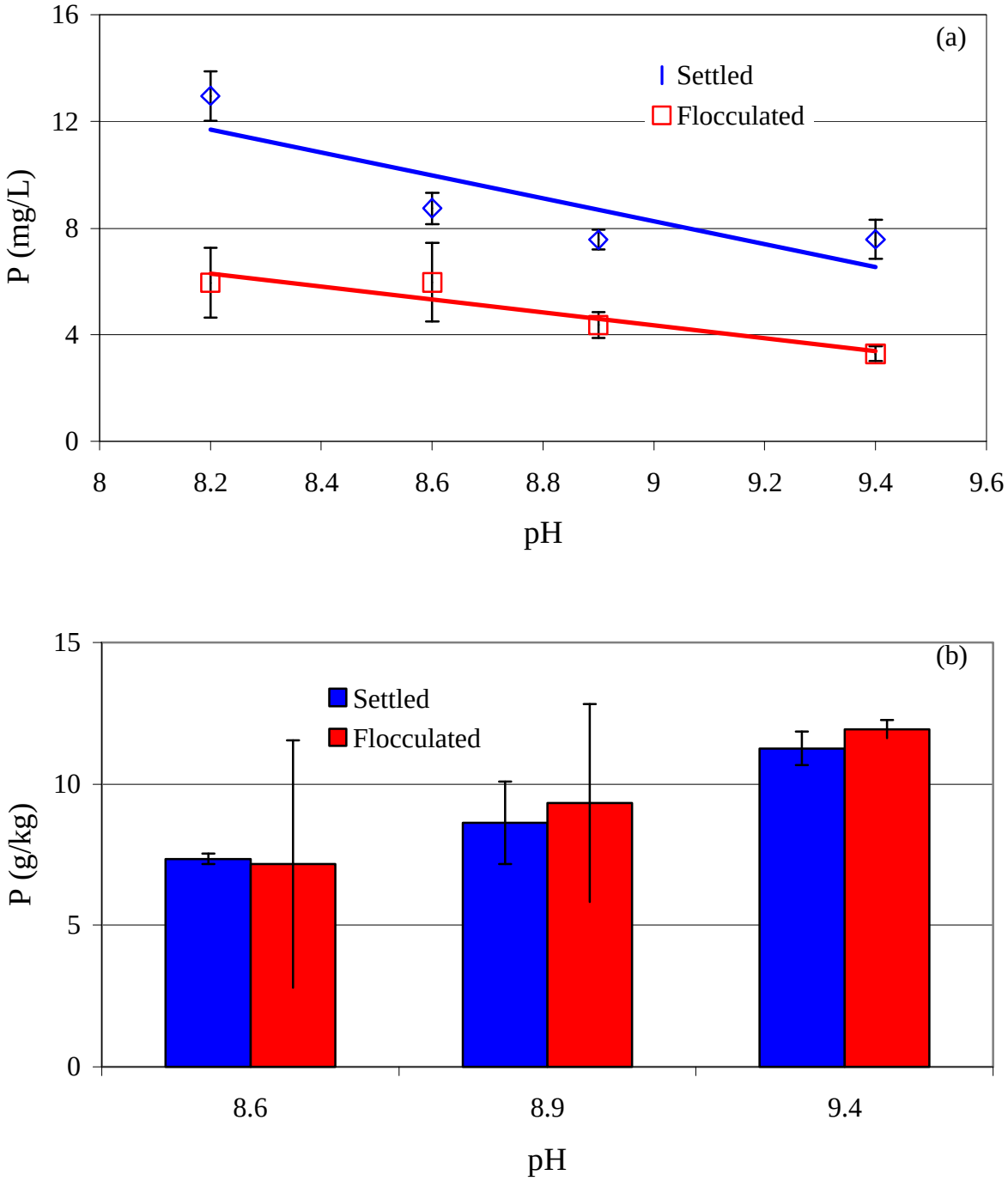


Figure 12: Changes in the P concentration of (a) the solution (mg L^{-1}) and (b) the precipitate (g kg^{-1}) with pH.

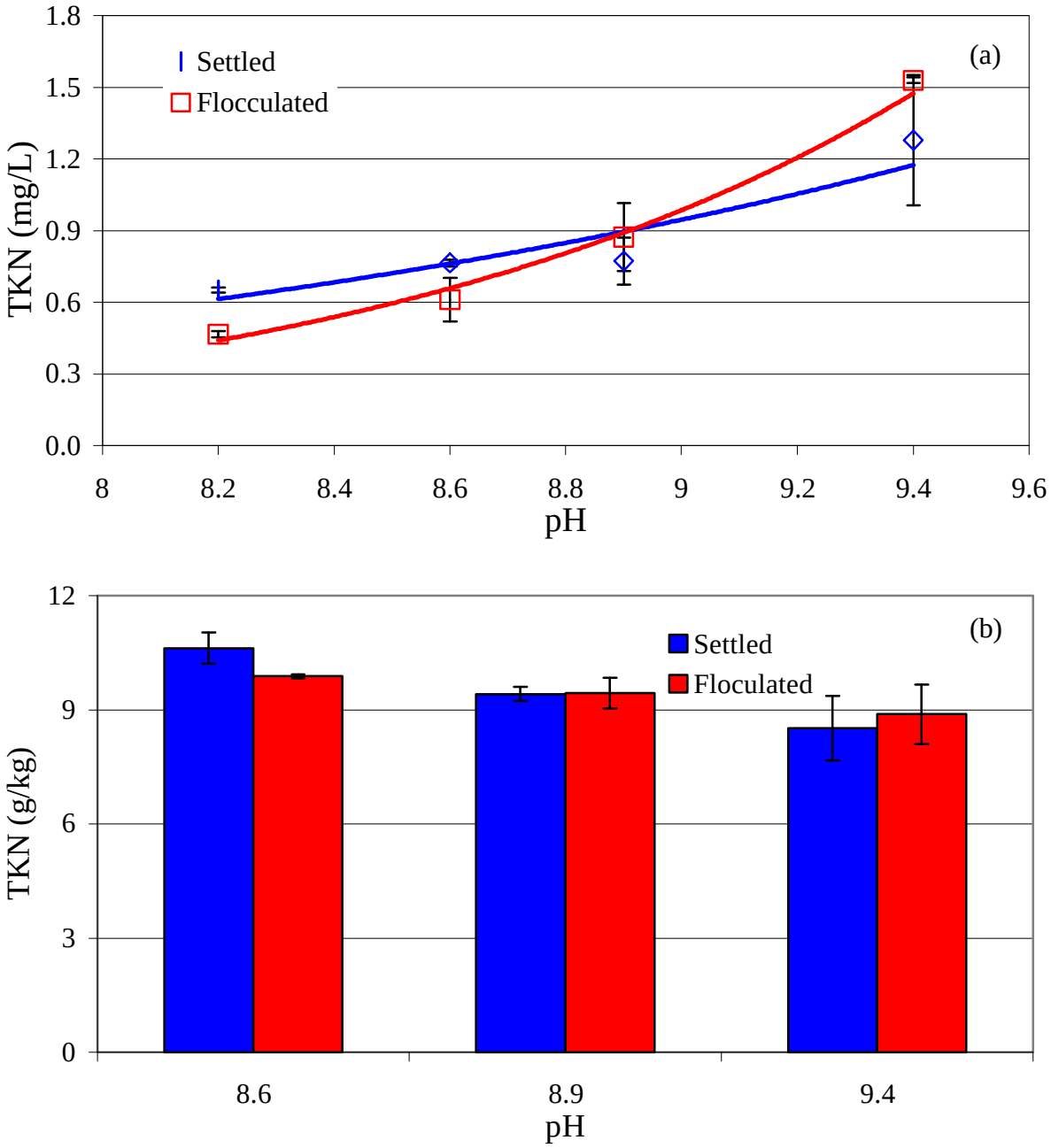


Figure 13: Changes in N concentrations (a) in the effluent (g/L) and (b) in the precipitate (g/kg) with pH.

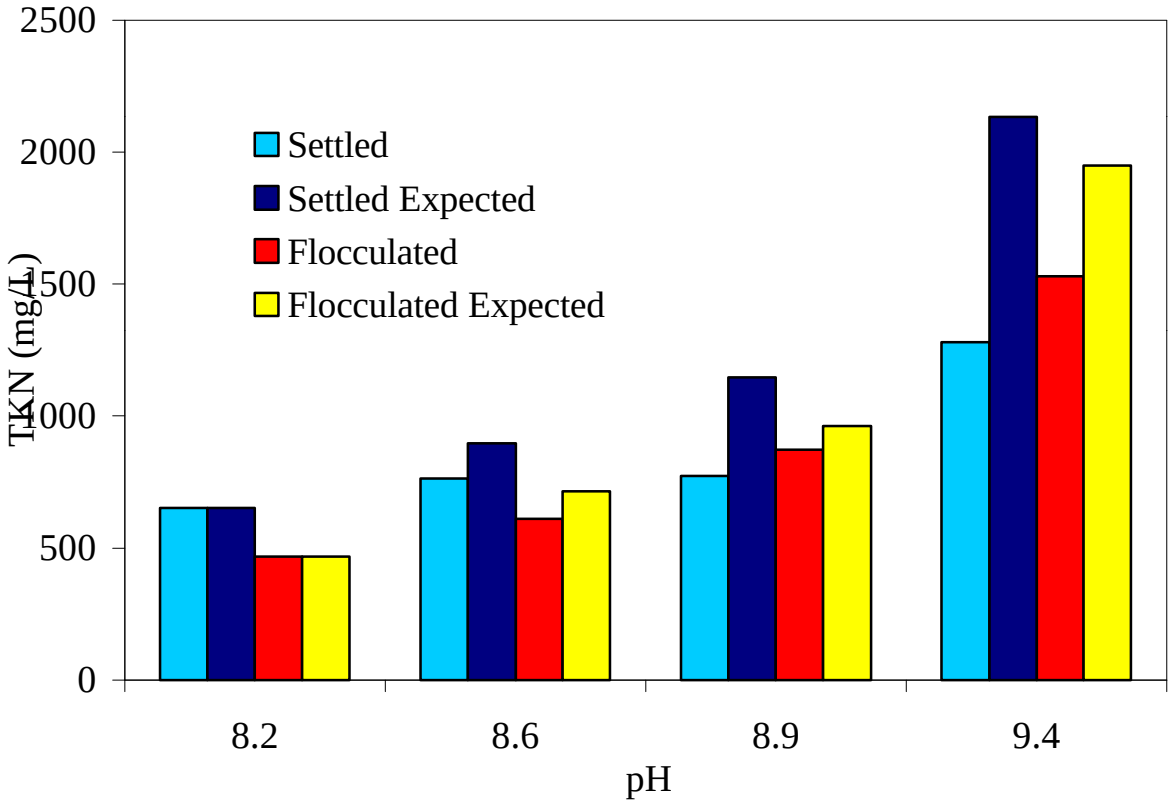
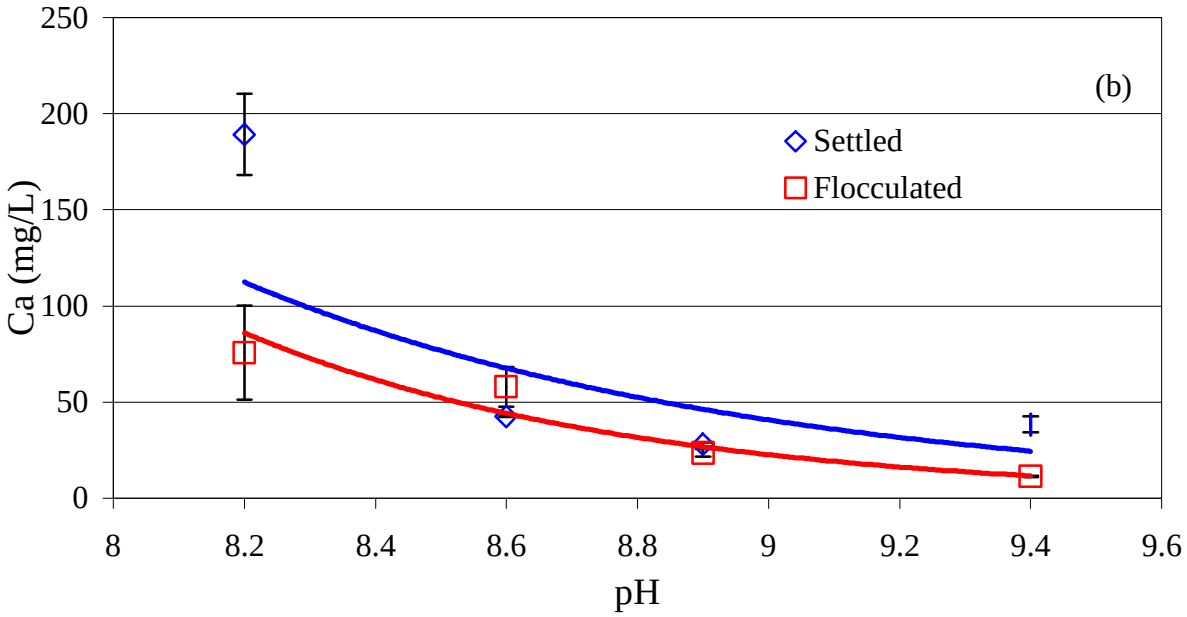


Figure 14: Changes in the actual TKN concentrations in the effluent as ammonium hydroxide was added to raise the pH compared to the expected total N rise attributed to the ammonium hydroxide addition.



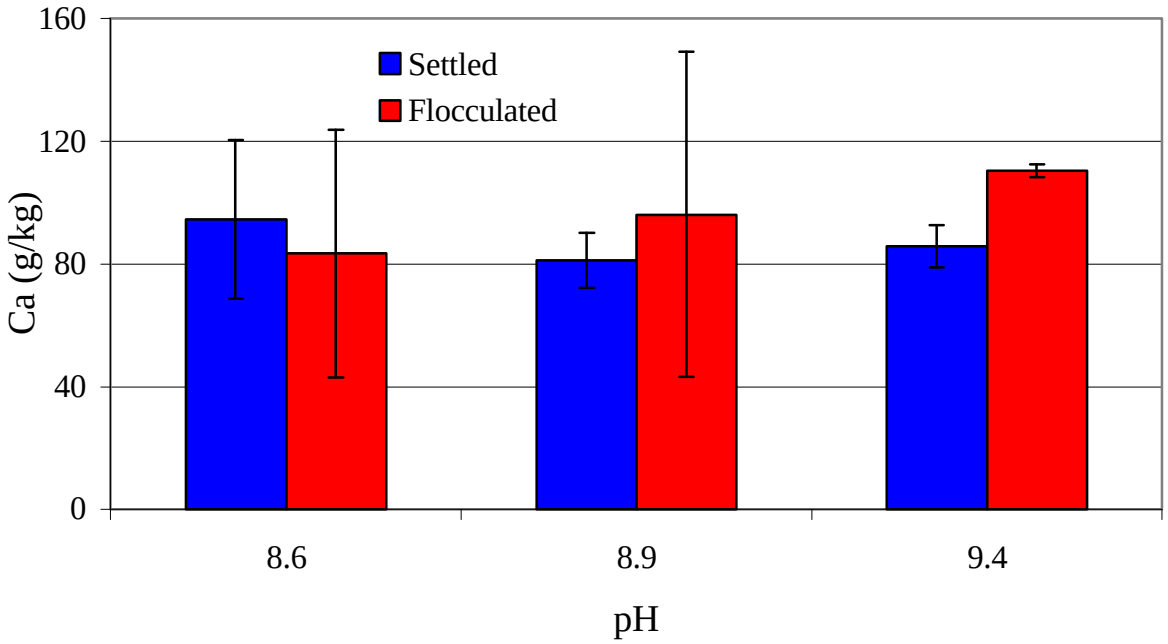


Figure 15: Changes in Ca concentrations (a) in the effluent (mg L^{-1}) and (b) in the precipitate (g kg^{-1}) with pH.

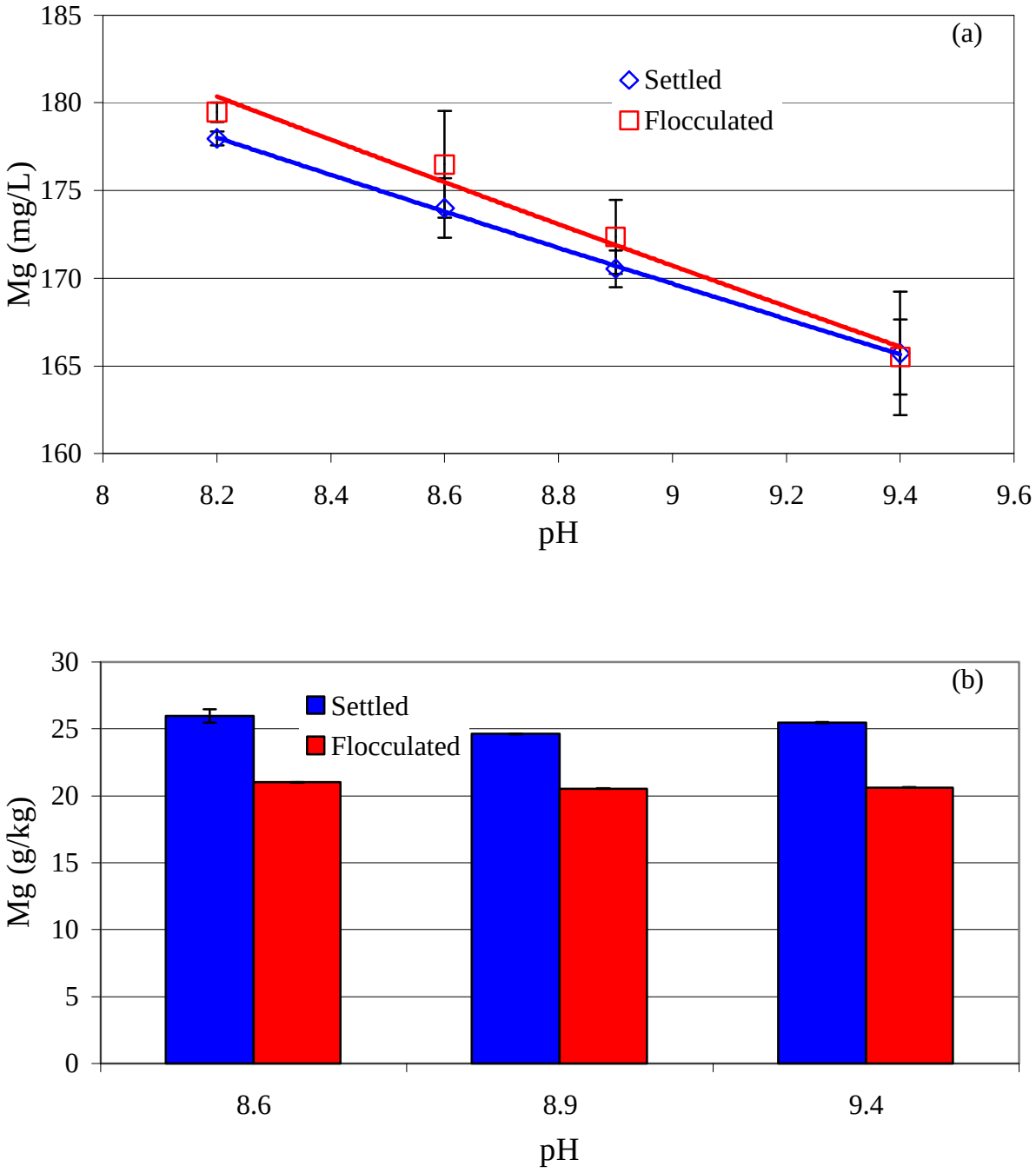


Figure 16: Changes in Mg concentrations (a) in the effluent (mg L^{-1}) and (b) in the precipitate (g kg^{-1}) with pH.

Table 5: Average concentrations of Cu, Fe, K, Mn, Na, and Zn and percent change in the flocculated and untreated effluent. All confidence intervals are for $\alpha = 0.05$. Corresponding graphs can be found in Appendix E – Characterization of the precipitates.

Element	pH 8.2	pH 8.6	pH 8.9	pH 9.4
	mg L^{-1} (% change)	mg L^{-1} (% change)	mg L^{-1} (% change)	mg L^{-1} (% change)
Cu–Untreated	0.146 ± 0.001 (0)	0.145 ± 0.015 (-1)	0.116 ± 0.005 (-21)	0.112 ± 0.022 (-23)
Cu–Flocculated	0.044 ± 0.007 (-70)	0.068 ± 0.006 (-53)	0.056 ± 0.005 (-62)	0.062 ± 0.024 (-58)
Fe–Untreated	4.092 ± 0.255 (0)	3.239 ± 1.401 (-21)	2.855 ± 1.247 (-30)	2.043 ± 0.382 (-50)
Fe–Flocculated	2.978 ± 3.930 (-27)	1.747 ± 0.735 (-57)	0.934 ± 0.190 (-77)	2.299 ± 2.682 (-43)
K–Untreated	1057 ± 16 (0)	1049 ± 10 (-1)	1034 ± 10 (-2)	1007 ± 26 (-5)
K–Flocculated	1067 ± 6 (+1)	1063 ± 12 (+1)	1048 ± 10 (-1)	1024 ± 12 (-3)
Mn–Untreated	0.193 ± 0.025 (0)	0.132 ± 0.001 (-32)	0.124 ± 0.008 (-36)	0.133 ± 0.012 (-31)
Mn–Flocculated	0.169 ± 0.042 (-12)	0.216 ± 0.061 (+12)	0.162 ± 0.009 (-16)	0.139 ± 0.032 (-28)
Na–Untreated	282.4 ± 4.9 (0)	283.6 ± 2.2 (+1)	277.0 ± 5.2 (-2)	267.8 ± 2.8 (-5)
Na–Flocculated	287.9 ± 3.7 (+2)	312.9 ± 43.9 (+10)	286.0 ± 5.4 (+1)	278.1 ± 5.8 (-2)
Zn–Untreated	0.607 ± 0.024 (0)	0.575 ± 0.023 (-5)	0.524 ± 0.018 (-14)	0.494 ± 0.016 (-18)
Zn-Flocculated	0.191 ± 0.027 (-69)	0.223 ± 0.020 (-63)	0.196 ± 0.019 (-68)	0.180 ± 0.013 (-70)

Table 6: Average concentrations of Cu, Fe, K, Mn, Na, and Zn and percent change in the precipitates from effluent where the solids had been removed by flocculation and sieving or by sieving alone as the pH of the effluent was increased. All confidence intervals are for $\alpha = 0.05$. Corresponding graphs can be found in Appendix E – Characterization of the precipitates.

Element	pH 8.6	pH 8.9	pH 9.6
	mg/kg (% change)	mg/kg (% change)	mg/kg (% change)
Cu–Untreated	17.48 ± 2.77 (0)	23.99 ± 16.86 (+37)	50.36 ± 22.60 (+188)
Cu–Flocculated	19.10 ± 0.75 (+10)	17.41 ± 3.60 (0)	18.95 ± 5.86 (+8)
Fe–Untreated	1153 ± 49 (0)	751 ± 458 (-34)	1147 ± 230 (-1)
Fe–Flocculated	696 ± 92 (-40)	789 ± 265 (+32)	715 ± 199 (+38)
K–Untreated	170510 ± 106139 (0)	93488 ± 7256 (-45)	80882 ± 17099 (-53)
K–Flocculated	75560 ± 74 (-56)	63387 ± 15171 (-63)	55414 ± 6977 (-68)
Mn–Untreated	108.65 ± 23.60 (0)	112.80 ± 7.74 (+4)	120.57 ± 8.32 (+11)
Mn–Flocculated	103.95 ± 0.88 (-4)	128.40 ± 10.70 (+18)	119.17 ± 19.55 (+10)
Na–Untreated	30601 ± 3185 (0)	24649 ± 1977 (-19)	21756 ± 5248 (-29)
Na–Flocculated	21012 ± 686 (-31)	16814 ± 4851 (-45)	14213 ± 2313 (-54)
Zn–Untreated	92.85 ± 1.68 (0)	83.27 ± 12.28 (-10)	106.70 ± 27.82 (-15)
Zn-Flocculated	66.90 ± 0.80 (-28)	70.20 ± 8.24 (-24)	65.13 ± 15.75 (-30)

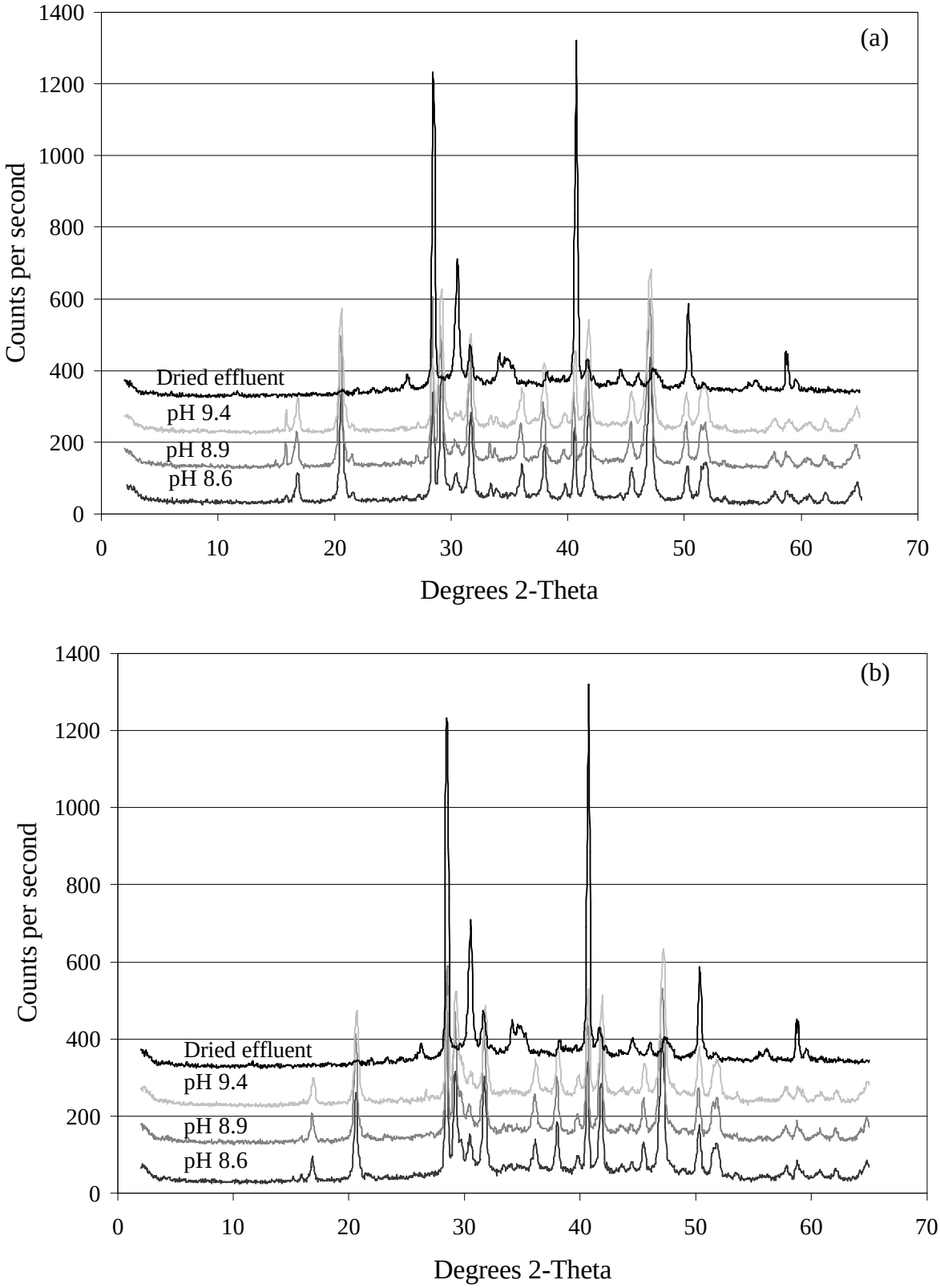


Figure 17: XRD patterns for (a) the flocculated and (b) the untreated precipitates.

CHAPTER V

DISCUSSION

Study 1 – Effect of settling

Settling, as a mechanism of solids separation, is slow and results in accumulation of solids and consequently an accumulation of P and other nutrients in the storage lagoon. The closed-system settling used for this experiment may give slightly misleading results in favor of use of settling as a management tool to separate solids. In an open system such as a lagoon, additions of fresh effluent and wind currents would limit some of the settling thus limiting the reduction of P associated with the settling particles. In addition, the portion of P that does settle with solids could become available for plant growth over time. To completely eliminate the potential for the settled P at the bottom of the lagoon to become available the lagoon must be dredged thus removing the settled solids.

While the changes in N concentrations might suggest that little N is associated with the solids, the rate of N mineralization was not tested in these studies, and it could be near the rate of settling. Equal mineralization and settling rates would lead the same amount of N being applied to the field through irrigation despite settling time. The large decrease in Ca and Mg concentrations early in the settling process suggests that much of the Ca and Mg are associated with the larger solid particles that settle quickest.

Study 2 – Flocculation

The data shown suggests that rapid removal of solids with flocculants might be used to keep solids from entering the lagoon. Some of the flocculated solids could be separated by the mechanical screens or be captured in a settling pond before entering the lagoon. As time passed, flocculant was less effective at reducing P. At flocculant concentrations of 1.3 mg L^{-1} and 3.73 mg L^{-1}, waiting for some of the larger solids to settle was of little advantage in reducing P concentrations; consequently, the earlier the flocculant could be added to the effluent stream, the greater the potential P removal. The decrease in flocculant efficiency over time might be a result of microorganisms decomposing the organic solids which increases the surface area of the solids; since surface area is directly related with reactivity. While the solids would be more reactive, more flocculant would be needed to produce the same decrease in suspended solids and those nutrients related to the suspended solids such as P. Particle size impacted the amount of chemical treatment required (Adin and Asano, 1998; Dao and Daniel, 2002). The presence of organic matter raises the flocculant demand because cationic PAM reacts preferentially with organic matter (Narkis and Rebhun, 1997). Treating effluents with flocculants earlier could maximize potential for removal of solids and the solid-associated elements.

Phosphorus, Zn, and Cu concentrations are closely related to the suspended particles in the effluent that are removed by the flocculant resulting in decreases in these elements with increased flocculant concentration. The effectiveness of using polymer combinations to reduce concentrations of ammonium, phosphate, TP, and pathogens in wastewater supports the use of polymers for treating dairy wastewater (Dao and Daniel, 2002; Entry and Sojka, 2000).

The lack of effect of flocculant Na, K, Ca, Fe, and Mg concentrations indicates that they are predominately in soluble forms.

Study 3 – Properties of the solids

Water holding capacity is directly related to pore size distribution and surface area. Finer textured materials are able to hold more water than coarse textured soils because they have smaller, more frequent void spaces. Since the flocculated solids can hold 0.2 more kg of water per kg of solid, the flocculated solids contain more fine particles than the untreated solids. Flocculation removed more fine solids than settling. Other studies have shown that polymers were more effective and could be a cost-effective replacement for alum treatment (Rout et al., 1999). The finer particles recovered by the flocculation treatment would account for the difference in solid mass recovered and for the difference in water holding capacity. Those elements removed from the solution with increasing flocculant concentrations are probably associated with these finer particles. Composts made with flocculated solids, which contained these finer solids, would be more valuable nutritional supplements and would increase the water holding capacity of the soil to which its applied more than composts that are made with dredged and mechanically separated solids. Recovery of the solids was done more meticulously than in field settings due to lower flow rates, clogging of the mesh, and the settling time allowed for the untreated materials prior to screening. Adin and Asano (1998) found that filtration efficiency was proportional to polymer doses. In a field setting, greater differences would be expected between untreated and treated solids.

Study 4 – Precipitation

Ammonium hydroxide was used to raise the pH because it is widely available and because equipment and handling problems exist with using other bases such as lime. Since ammonium hydroxide was used to raise the pH the N concentrations in the solution increased with increased pH. Phosphorus and Ca concentrations decreased dramatically in the solution with the increase in pH suggesting that the soluble Ca and P joined to form the predominate precipitate. van Rensburg et al. (2003) found that struvite precipitated in anaerobic digester liquors with only small amounts of amorphous calcium phosphate precipitating. Other studies have also shown struvite precipitation under anaerobic conditions (Battisoni et al,. 2000; Nelson et al., 2003; Schuiling and Andrade, 1999). The effluent in this study was not kept under strictly anaerobic conditions; this difference in aerobic vs. anaerobic conditions might explain why struvite was not a dominant precipitate. Stumm and Morgan (1981) found precipitation of struvite in aerobic systems to be unlikely. Magnesium, K, Mn, Na, and Zn concentrations also decreased, but to a lesser extent, indicating they were less likely to be found in the precipitates.

Study 5 – Characterization of the precipitates

Copper, Fe, and Zn did not change with increases in the solution pH, so it is logical to assume that these elements did not precipitate. Phosphorus, Ca, K, Na, and Mg decreased in the solution as the pH increased. Studying the elements that decreased in the solution as the pH increased, it would appear that P precipitated as both calcium and magnesium phosphates. Since larger quantities of Ca were removed from the solution as the pH increased, the calcium phosphates were most prevalent. Several studies support the precipitation of calcium

phosphates at pHs above 8 (Angel, 1999; Carlsson et al., 1997; House, 1999; Song et al., 2002).

X-ray diffraction data indicated the presence of monohydrocalcite ($CaCO_3*H_2O$), calcium phosphate ($Ca_3(PO_4)_2$), sylvite (KCl), halite (NaCl), and possibly struvite ($MgNH_4PO_4*6H_2O$). The decreases in Ca, K, Na, Mg, and P concentrations in the solution support the presence of these minerals. While halite and sylvite precipitation does not result in P removal, it does decrease the salt concentration in the effluent to be used for irrigation. In dialyzed samples, these salts do not precipitate. The decrease in Ca concentration supports the presence of both mono-hydrocalcite and calcium phosphate. Both of these minerals form at higher pH's. While traces of struvite are indicated by the XRD patterns, the amount of precipitated struvite based on differences in Mg concentrations is minimal. Numerous phosphate compounds may precipitate. While calcium phosphate may not be as useful as other-P compounds, such as struvite, research shows that they can be precipitated with fewer inputs and under aerobic conditions.

Visual MINTEQ (Royal Institute of Technology, 2003) was used predict which minerals would be the most likely to precipitate (*see Appendix F – Visual MINTEQ*). The main predicted precipitates based on saturation indexes (SI) were calcium phosphates. Calcium magnesium carbonates had the next highest SI. Calcium carbonates had the second to lowest SI, and magnesium carbonates had the lowest SI of oversaturated minerals. No magnesium phosphates were indicated as oversaturated. These findings support the precipitation of calcium phosphates

Implications

To determine the significance of the research, it is essential to understand how it could impact the dairy producers. A highly loaded soil in the Bosque River watershed typically has 10 mg kg^{-1} NO_3-N, 300 mg kg^{-1} P, and 600 mg kg^{-1} K. Production of coastal bermuda hay production (6 tons $acre^{-1}$ $year^{-1}$) removes 240 kg ha^{-1} N, 18 kg ha^{-1} P, and 180 kg ha^{-1} K, and winter wheat produced for hay (2 tons $acre^{-1}$ $year^{-1}$) removes 120 kg ha^{-1} N, 18 kg ha^{-1} P, and 120 kg ha^{-1} K (Mills and Jones, 1996). Summer and winter hay systems combined can mine the soil nutrients throughout the year.

Raw effluent from this study had initial concentrations of 660 mg L^{-1} N, 76 mg L^{-1} P, and 1158 mg L^{-1} K. Raw effluent would increase P 66 $year^{-1}$ ha^{-1} if applied to this soil at the agronomic N-rate (**Figure 18**). Applying the effluent at the P crop requirement rate however would fail to supply the crops N requirements.

Effluent with 3.73 mg L^{-1} flocculant would have 492 mg L^{-1} N, 26.3 mg L^{-1} P, and 1094 mg L^{-1} K. Since the flocculated effluent has lower concentrations of nutrients than the raw effluent, more flocculated effluent can be applied to the land than raw effluent. The effluent applications at the agronomic N rate would result in a decrease in soil surface P by 8 kg $year^{-1}$ ha^{-1}.

Effluent treated with flocculant and ammonium hydroxide would have a nutrient composition of 1041 mg L^{-1} N, 1.62 mg L^{-1} P, and 1004 mg L^{-1} K. If the effluent was applied to the soil at the agronomic N-rate, the P concentration in the soil surface would decrease 35 kg $year^{-1}$ ha^{-1}. In eight years, the soil surface P concentrations would be negligible from a P pollution standpoint.

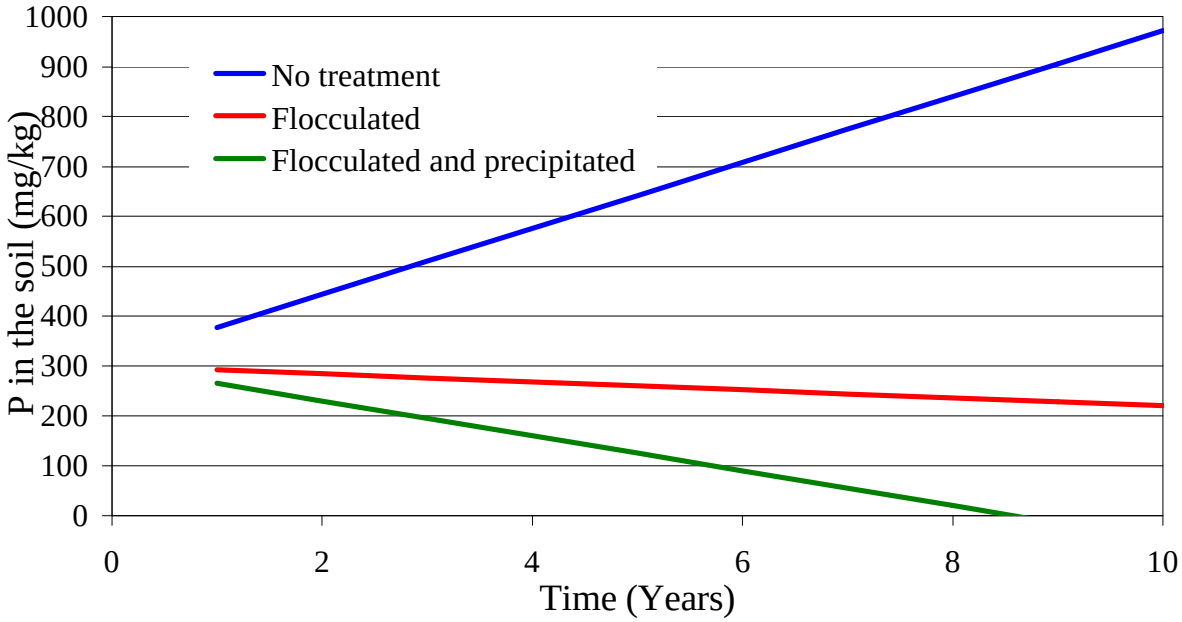


Figure 18: Changes in soil surface P with time and effluent management cultivated under Coastal Bermuda / Winter Wheat forage system.

CHAPTER V

SUMMARY

The growing need for P recovery from wastes and the continuing problems with surface water quality issues make managing P essential. While P is an essential and often limiting nutrient for plant growth, over-applications of P in effluents and manures result in P buildups. Eventually the P enters water bodies where it causes algal blooms.

Flocculation can provide a quick and effective means of reducing P concentrations to manageable concentrations (from near 80 to <20 mg L^{-1}). Precipitation can be used to further reduce P concentrations (from 20 to < 3 mg L^{-1}). Combining flocculation with precipitation allows for maximal removal of P from effluents (final concentration <3 mg L^{-1}). At levels <3 mg L^{-1} (a greater than 95% total reduction) effluent management would be independent of P. Future research should include: Cost analysis of flocculation/precipitation treatments; analysis of the solids as a soil amendment and as compost; and large scale studies to determine the potential for using flocculation/precipitation on a working dairy operation.

REFERENCES

Adin, A., and T. Asano. 1998. The role of physical-chemical treatment in wastewater reclamation and reuse. Water Sci. Technol. 37(10):79-90.

Adler, J.A. 1994. International anthropogenic methane emissions: Estimates for 1990. Report to Congress. EPA Report 230R93010, p. 332.

Angel, R. 1999. Removal of phosphate from sewage as amorphous calcium phosphate. Environ. Technol. 20:709-720.

Barker, J.C., J.P. Zublena, and C.R. Cambell. 1994. Agri-waste management: Livestock manure production and characterization in North Carolina. NC Cooperative Extension Service, North Carolina State University.

Battistoni, P., G. Fava, P. Pavan, A. Musacco, and F. Cecchi. 1997. Phosphate removal in anaerobic liquors by struvite crystallization without the addition of chemicals: Preliminary results. Water Res. 31:2925-2929.

Bowker, R.P.G., and H.D. Stensel. 1990. Phosphorus removal from wastewater. Pollution Technology Review No. 189. Noyes Data Corp., Park Ridge, NJ.

Buchanan, J.R., C.R. Mote, and R.B. Robinson. 1994. Struvite control by chemical treatment. Trans. ASAE 37(4):1301-1308.

Carlsson, H., H. Aspengren, N. Lee, and A. Hilmer. 1997. Calcium phosphate precipitation in biological phosphorus removal systems. Water Res. 31(5):1047-1055.

Carpenter, S.R., N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, and V.H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Applic. 8:559-568.

Cecchi, F., P. Battistoni, P. Pavan, G. Fava, and J. Mata-Alverez. 1994. Anaerobic digestion of OFMSW (Organic fraction of solid waste) and BNR (Biological nutrient removal) processes: A possible integration – Preliminary results. Water Sci. Technol. 30(8):65-72.

Cheremisinoff, N. P. 1994. Biomanagement of wastewaters and wastes. PTR Prentice Hall, Englewood Cliffs, NJ.

Cheremisinoff, N.P. 2002. Handbook of water and wastewater treatment technologies. Butterworth-Heinemann, Boston, MA.

Choi, E., S.W. Oa, and J.J. Lee. 1997. Nightsoil treatment plant converted into a sequencing batch reactor to improve removal of pollutants and nutrients. Water Sci. Technol. 35:233-240.

Correll, D.L. 1998. The role of phosphorus in the eutrophication of receiving waters: A review. J. Environ. Qual. 27:261-266.

Council for Agricultural Science and Technology. 1996. Integrated animal waste management. Task Force Rep. 128 CAST, Ames, IA.

Cronk, J.K. 1996. Constructed wetlands to treat wastewater from dairy and swine operations: A review. Agric. Ecosyst. Environ. 58:97-114.

Dagnall, S., J. Hill, and D. Pegg. 2000. Resource mapping and analysis of farm livestock manures – assessing the opportunities for biomass-to-energy schemes. Bioresourc. Technol. 71:225-234.

Daniel, T.C., A.N. Sharpley, D.R. Edwards, R. Wedepohl, and J.L. Lemunyon. 1994. Minimizing surface water eutrophication from agriculture by phosphorus management. J. Soil Water Conserv. Suppl. 49:30-38.

Dao, T.H., and T.C. Daniel. 2002. Particulate and dissolved phosphorus chemical separation and phosphorus release from dairy manure. J. Environ. Qual. 31:1388-1398.

Dierg, F.E., and P.L. Brezonik. 1983. Nitrogen and phosphorus mass balances in natural and sewage-enriched cypress domes. J. Appl. Ecol. 20:323-337.

Doyle, J.D., and S.A. Parsons. 2002. Struvite formation, control and recovery. Water Res. 36:3925-3940.

Drinan, J.E. 2001. Water & wastewater management: A guide for the nonengineering professional. Technomic Publishing Co., Inc. Lancaster, PA.

Driver, J., D. Lijmbach, and I. Steen. 1999. Why recover phosphorus for recycling, and how? Environ. Technol. 20:651-662.

Droste, R.L. 1997. Theory and practice of water and wastewater treatment. John Wiley & Sons, Inc. New York, NY.

Edwards, A.C., H. Twist, and G.A. Codd. 2000. Assessing the impact of terrestrially derived phosphorus on flowing water systems. J. Environ. Qual. 29:117-124.

Entry, J.A., and R.E. Sojka. 2000. The efficacy of polyacrylamide and related compounds to remove microorganisms and nutrients from animal wastewater. J. Environ. Qual. 29:1905-1914.

Foy, R.H., and A.E. Watts. 1998. Observations on the spatial and temporal variations in the phosphorus status of lakes in the British Isles. Soil Use Manage. 14:131-138.

Franklin, S.T., K.R. Martin, R.J. Baer, D.J. Schingoethe, and A.R. Hippen. 1999. Dietary marine algae (*Schizochytrium* sp.) increases concentrations of conjugated linoleic, docosahexaenoic and transvaccenic acids in milk of dairy cows. J. Nutr. 129(11):2048-2054.

Frossard, E., S. Sinaji, and P. Dufour. 1996. Phosphorus in urban sewage sludges as assessed by isotropic exchange. Soil Sci. Soc. Am. J. 60:179-184.

Gaterell, M.R., R. Gay, R. Wilson, R.J. Gochin, and J.N. Lester. 2000. An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertilizer markets. Environ. Technol. 21:1067-1084.

Greaves, J., P. Hobbs, D. Chadwick, and P. Haygarth. 1999. Prospects for the recovery of phosphorus from animal manures: A review. Environ. Technol. 20:697-708.

Grimm, A. 1972. Dairy manure waste handling systems. p. 124-144. *In* Proceedings of the 1972 Cornell Agricultural Waste Management Conference. Graphics Management Corp., Washington, DC.

Gunn, D.J. 1976. Mechanism for the formation and growth of ionic precipitates from aqueous solution. Faraday Discuss. Chem. 61:133-140.

Ham, J.M. 2003. Personal communication. Professor – Soil Physics. Kansas State University.

Hammer, D.A. 1992. Creating freshwater wetlands. Lewis Publishers, Inc. Chelsea MI.

Hamoda, M., and S. Al-Awadi. 1996. Improvement of effluent quality for reuse in a dairy farm. Water Sci. Technol. 33(10-11):79-85.

Haygarth, P.M., and A.N. Sharpley. 2000. Terminology for phosphorus transfer. J. Environ. Qual. 29:10-15.

Heathwaite, A.L., A.N. Sharpley, and W.J. Gburek. 2000. A conceptual approach for integrating phosphorus and nitrogen management at watershed scales. J. Environ. Qual. 29:158-166.

Hoogwijk, M., A. Faaij, R van den Broek, G. Bernedes, D. Gielen, and W. Turkenburg. 2003. Exploration of the ranges of the global potential of biomass for energy. Biomass & Bioenergy 25:119-133.

House, W.A. 1999. The physico-chemical conditions for the precipitation of phosphate with calcium. Environ. Technol. 20: 727-733.

Jacoby, J.M., D.D. Lynch, E.B. Welch, and M.S. Perkins. 1982. Internal phosphorus loading in a shallow eutrophic lake. Water Res. 16:911–919.

Jaworski, N.A., P.M. Groffman, A.A. Keller, and J.C. Prager. 1992. A watershed nitrogen and phosphorus balance: The Upper Potomac River Basin. Estuaries 15:83-95.

Johnson, J.C. Jr., G.L. Newton, J.L Butler. 1991. Recycling liquid dairy cattle waste to sustain annual triple crop production of forages. p. 41-50. *In* Proceedings of the 28th Annual Florida Dairy Production Conference. Dairy Science Department, University of Florida, Gainesville, FL.

Johntson, C.A., G.D. Bubenzer, G.B. Lee, F.W. Madison, and J.R. McHenry. 1984. Nutrient trapping by sediment deposition in a seasonably flooded lakeside wetland. J. Environ. Qual. 13:283-290.

Joint Committee on Powder Diffraction Standards. 1974. Selected powder diffraction data for minerals: search manual. Joint Committee on Powder Diffraction Standards and American Society for Testing and Materials, Swarthmore, PA.

Kashmanian, R.M. 1994. Building support for composting in agriculture. Biocycle, 35(12):67-70.

Kelling, K.A., L.M. Walsh, D.R. Keeny, J.A. Ryan, and A.E. Peterson. 1977. A field study of the agricultural use of sewage sludge: Effect on soil N and P. J. Environ. Qual. 6:345-352.

Kirkham, M.B. 1982. Agricultural use of phosphorus in sewage sludges. Adv. Agron. 35:129-163.

Klauss, D.L. 1984. Fuels from biomass. p. 32-90. *In* M. Grayson (ed.) Recycling, fuel and resource recovery: Economic and environmental factors. Wiley-Interscience, New York.

Knight, R.L., T.W. McKim, and H.R. Kohl. 1987. Performance of a natural wetland system for wastewater management. J. Water Pollut. Control Fed. 59:746-754.

Leedan, F., F. Troise, and D. Todd. 1990. The water encyclopedia. 2nd ed. Lewis Publ. New York.

Lentz, R.D., I. Shainberg, R.E. Sojka, and D.L. Carter. 1992. Preventing irrigation furrow erosion with small applications of polymers. Soil Sci. Soc. Am. J. 56:1926-1932.

Lentz, R.D., and R.E. Sojka. 1994. Field results using polyacrylamide to manage furrow erosion and infiltration. Soil Sci. 158:274-282.

Letterman, R.D., A. Amirththarajah, and C.R. O'Melia. 1999. Coagulation and flocculation. p. 6.1-6.66. *In* R.D. Letterman (ed.) Water quality and treatment. 5th ed. McGraw-Hill, New York.

Levine, D.A., G. Tchobanoglous, and T. Asano. 1986. Characterization of the size distribution on contaminants in wastewater treatment and reuse implications. J. Water Pollut. Control Fed. 57(7):805-816.

Liberti, L., N. Limoni, A. Lopez, R. Passino, and G. Boari. 1986. The 10 m^3 h^{-1} RIM-NUT demonstration plant at West Bari for removing and recovering N and P from wastewater. Water Res. 20:735-739.

Little, C.E. 1998. Rural clean water: The Okeechobee story. J. Soil Water Conserv. 43:386-390.

Loehr, R.C. 1974a. Agricultural waste management problems, processes, and approaches. Academic Press, New York.

Loehr, R.C. 1974b. Characteristics and comparative magnitude of nonpoint sources. J. Water Pollut. Control Fed. 46:1849-1870.

Maguire, R.O., J.T. Sims, and F.J. Coale. 2000. Phosphorus solubility in biosolid-amended farm soils in the Mid-Atlantic region of the USA. J. Environ. Qual. 29:1225-1233.

Mangraviter, F.J.Jr., C.R. Leitz, and D.J. Juvan. 1978. Application of polyelectrolytes for industrial sludge dewatering. p. 268-281. *In* A.J. Rubin (ed.) Chemistry of wastewater technology. Ann Arbor Science. Ann Arbor, MI.

McCoy, J.L., J. Sikora, and R.R. Weil. 1986. Plant availability of phosphorus in sewage sludge. J. Environ. Qual. 15:403-409.

McFarland, A.M.S., and L.M. Hauck. 1999. Relating agricultural land uses to in-stream stormwater quality. J. Environ. Qual. 28:836–844.

Mills, H.A. and J.B. Jones, Jr. 1996. Plant analysis handbook II: A practical sampling, preparation, analysis, and interpretation guide. MicroMacro Publishing, Inc. Athens, GA.

Miner, J.R., F.J. Humenik, and M.R. Overcash. 2000. Managing livestock wastes to preserve environmental quality. Iowa State University Press, Ames, IA.

Nancollas, G.H., M.B. Tomson, G. Battaglia, H. Wawrousek, and M. Zuckerman. 1978. Precipitates of calcium phosphates: the influence of tricarboxylic acids, magnesium, and phosphate. p. 17-30. *In* A.J. Rubin (ed.) Chemistry of wastewater technology. Ann Arbor Science. Ann Arbor, MI.

Narkis, N., and M. Rebhun. 1997. Flocculation in presence of organic macromolecules of natural water and secondary effluents. Water Sci. Technol. 36 (4), 85-91.

National Academy of Sciences. 1992. Conserving biodiversity: A research agenda for development agencies. National Academy Press, Washington, DC.

National Research Council. 1993. Soil and water quality: An agenda for agriculture. National Academy Press, Washington, DC.

Nelson, D.W., and L.E. Sommers. 1973. Determination of total nitrogen in plant material. Agron. J. 65:109-112.

Nelson, D.W., and L.E. Sommers. 1980. Total nitrogen analysis of soil and plant tissues. J. Assoc. Off. Anal. Chem. 63(4):770-778.

Nelson, N.O., R.L. Mikkelsen, and D. L. Hesterberg. 2003. Struvite precipitation in anaerobic swine lagoon liquid: Effect of pH and Mg:P ratio and determination of rate constant. Bioresourc. Technol. 89:229-236.

Ohlinger, K.N., T.M. Young, and E.D. Schroeder. 1998. Predicting struvite formation in digestion. Water Res. 32:3607-3614.

Ohlinger, K.N., T.M. Young, and E.D. Schroeder. 1999. Kinetics effects on preferential struvite accumulation in wastewater. J. Environ. Eng. 124:730-737.

Ohlinger, K.N., T.M. Young, and E.D. Schroeder. 2000. Postdigestion struvite precipitation using a fluidized bed reactor. J. Environ. Eng. 126:361-368.

Outlaw, J., A. Purvis, and J. Miller. 1995. An evaluation of dairy manure management economics. AFPC Policy Research Report 95-2 Nov. 1995.

Parkinson, J.A., and S.E. Allen. 1975. A wet oxidation procedure suitable for the determination of nitrogen and mineral nutrients in biological material. Comm. Soil. Sci. Plant Anal. 6(1):1-11.

Parry, R. 1998. Agricultural phosphorus and water quality: A U.S. Environmental Protection Agency perspective. J. Environ. Qual. 27:258-261.

Penn, C.J. and J.T. Sims. 2002. Phosphorus forms in biosolids-amended soils and losses in runoff: Effects of wastewater treatment processes. J. Environ. Qual. 31:1349-1361.

Pietilainen, O.P. and S. Rekolainen. 1991. Dissolved reactive and total phosphorus loads from agricultural and forested basins to surface waters in Finland. Aqua Fennica 21:127-136.

Ramadori, E. (ed.) 1987. Biological phosphate removal from wastewaters: Proc. IAWPRC

Specialized Conf., Rome, Italy, 28-30 Sept. 1987. Pergamon Press, Oxford.

Reaves, R.P., P.J. DuBowy, and B.K. Miller. 1994. Performance of a constructed wetland for dairy waste treatment in Lagrange County, Indiana. p. 43-52. *In* P.J. DuBowy and R.P. Reaves (ed.) Proc. of a Workshop on Constructed Wetlands for Animal Waste Management, 4-6 April 1994, Lafayette, IN.

Rhyner, C.R., L.J. Schwartz, R.B. Wenger, and M.G. Kohrell. 1995. Waste management and resource recovery. CRC Press, Boca Raton, FL.

Rout, D., R. Verma, and S. Agarwal. 1999. Polyelectrolyte treatment – An approach for water quality improvement. Water Sci. Technol. 40 (2), 137-141.

Royal Institute of Techonology. 2003. Visual MINTEQ. Available at http://www.lwr.kth.se/english/OurSoftware/vminteq/index.htm (verified 19 Oct. 2003).

Sanderson, M.A., R.M. Jones, M.J. McFarland, J. Stroup, R.L. Reed, and J.P. Muir. 2001. Nutrient movement and removal in swtichgrass biomass-filter strip system treated with dairy manure. J. Environ. Qual. 30:210-216.

Schindler, D.W. 1977. Evolution of phosphorus limitation in lakes. Science 195:260-262.

Schuling, R.D., and A. Andrade. 1999. Recovery of struvite from calf manure. Environ. Technol. 20, 765-768.

Sharpe, R.R., L.A. Harper, and F.M. Byers. 2002. Methane emissions from swine lagoons in Southeastern US. Agric. Ecosyst. Environ. 90:17-24.

Sharpley, A.N., S.C. Chapra, R. Wedepohl, J.T. Sims, T.C. Daniel, and K.R. Reddy. 1994. Managing agricultural phosphorus for protection of surface waters: Issues and options. J. Environ. Qual. 23:437-451.

Sharpley, A.N., T.C. Daniel, J.T. Sims, and D.H. Pote. 1996. Determining environmentally sound soil phosphorus levels. J. Soil Water Conserv. 51:160-166.

Sharpley, A.N., J.J. Meisinger, A. Breeuwsma, T. Sims, T.C. Daniel, and J.S. Schepers. 1998. Impacts of animal manure management on ground and surface water quality. p. 173-242. *In* J. Hatfield (ed.) Effective management of animal waste as a soil resource. Ann Arbor Press, Chelsea, MI.

Shin, H.S., and S.M. Lee. 1997. Removal of nutrients in wastewater by using magnesium salts. Environ. Technol. 19:283-290.

Shindala, A., and M.T. Bond. 1978. Chemical treatment for nutrients and algal removal from oxidation pond effluents. p. 111-122. *In* A.J. Rubin (ed.) Chemistry of wastewater technology.

Ann Arbor Science. Ann Arbor, MI.

Sievers, D.M. 1997. Potential reduction of struvite formation from anaerobic swine lagoon effluent by treatment in constructed wetlands. Trans. ASAE, 40(3), 803-805.

Sims, J.T., R.R. Simard, and B.C. Joern. 1998. P losses in agricultural drainage: Historical perspective and current research. J. Environ. Qual. 27:277-293.

Smith, P.G., and J.S. Scott. 2002. Dictionary of water and waste management. IWA Publishing. London.

Snoeyink, V.L., and D. Jenkins. 1980. Water chemistry. Wiley-Interscience, New York.

Song, Y., H. Hahn, and E. Hoffmann. 2002. Effects of solution conditions on the precipitation of phosphate for recovery – A thermodynamic evaluation. Chemosphere 48:1029-1034.

Soon, Y.K., T.E. Bates, and J.R. Moyer. 1978. Land application of chemically treated sewage sludge: II. Effects on plant and soil phosphorus, potassium, calcium, magnesium, and soil pH. J. Environ. Qual. 7:269-273.

Stumm, W., and J.J. Morgan. 1970. Aquatic chemistry: An introduction emphasizing chemical equilibria in natural waters, 3rd ed. Wiley-Interscience, New York, 197-201.

Stumm, W., and J.J. Morgan. 1981. Aquatic chemistry: An introduction emphasizing chemical equilibria in natural waters, 2nd ed. Wiley, New York, 197-201.

Stratful, I., S. Brett, M.B. Scrimshaw, and J.N. Lester. 1999. Biological phosphorus removal, its role in phosphorus recycling. Environ. Technol. 20:681-695.

Sweeten, J.M., and M.L. Wolfe. 1993. The expanding dairy industry: Impact on ground water quality and quantity with emphasis on waste management systems evaluation for open lot dairies. TR-155, Texas Water Resources Institute, Texas A&M University System, College Station, TX.

Sweeten, J.M., and M.L. Wolfe. 1994. Manure and wastewater management systems for open lot dairy operations. Trans. ASAE 37:1145–1154.

Texas Water Commission and Texas State Soil and Water Conservation Board. 1991. 1990 update to the nonpoint source water pollution management report for the state of Texas. TWC and TSSWCB, Austin.

Tillman, D.A. 2000. Biomass cofiring: The techonology, the experience, the combustion consequences. Biomass & Bioenergy 19:365-384.

TNRCC. 1999. Improving water quality in the North Bosque River. TNRCC, Austin, Texas.

Tunney, H. 1988. A note on a balance sheet approach to estimating the phosphorus fertilizer needs of agriculture. Irish J. Agric. Res. 29:149-154.

USDA. 1996. Soil survey laboratory methods manual. Site Survey Investigations Report No. 42, Ver. 3.0, Washington, DC.

USDA and USEPA. 1998. Draft: Unified national strategy for animal feeding operations. USDA and USEPA, Washington, DC.

USDA National Agricultural Statistics Service. 2001. USDA-NASS hompage. Available online at http://www.usda.gov/nass (verified 2 Oct. 2003). USDA-NASS, Washington, DC.

U. S. Environmental Protection Agency. 1993. Municipal wastewater treatment technology: Recent developments. Noyes Data Corp. Park Ridge, NJ.

Wender, I., F.W. Steffgen, and P.M. Yavorsky. 1974. Clean liquid and gaseous fuels from organic solid wastes. p. 43-99. *In* T.F. Yen (ed.) Recycling and disposal of solid wastes: Industrial, agricultural, and domestic. Ann Arbor Science, Ann Arbor, MI.

Vanotti, M.B., and P.G. Hunt. 1999. Solids and nutrient removal from swine manure using polyacrylamides. Trans. ASAE 42:1833-1840.

van Rensburg, P., E.V. Musvoto, M.C. Wentzel, and G.A. Ekama. 2003. Modelling multiple mineral precipitation in anaerobic digester liquor. Water Res. 37:3087-3097.

Vorchheimer, N. 1981. Synthetic polyelectrolytes. p. 1-45. *In* Schwoyer, W.L.K. (ed.) Polyelectrolytes for Water and Wastewater Treatment. CRC Press, Boca Raton, FL.

Wilkie, A.C., and W.W. Mulbry. 2002. Recovery of dairy manure nutrients by benthic freshwater algae. Bioresourc. Technol. 84:81-91.

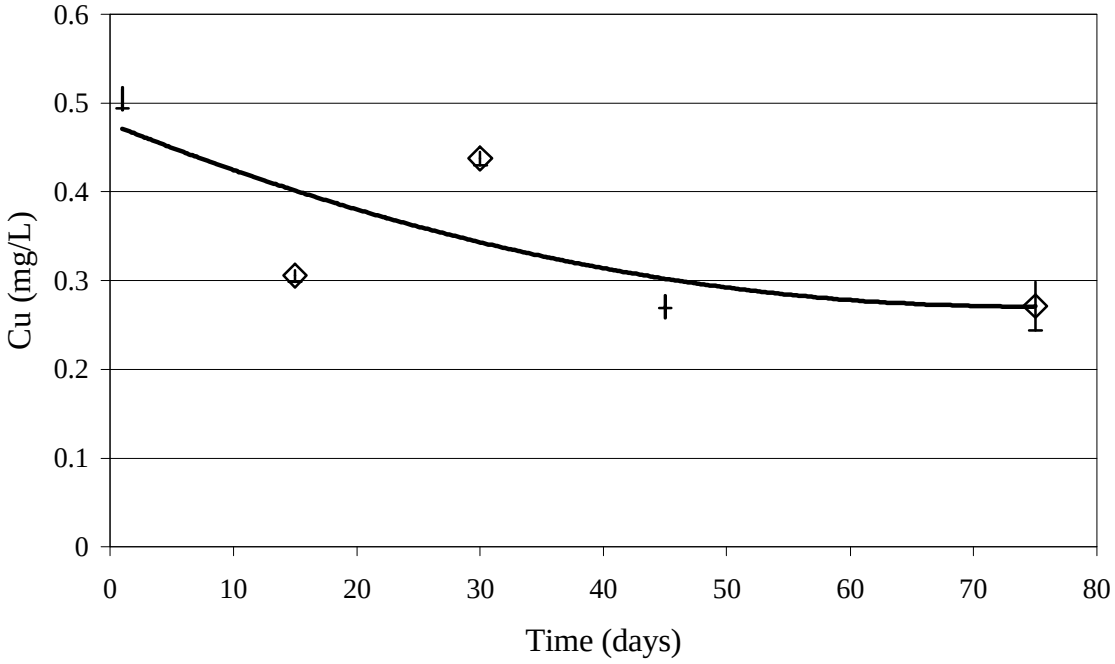
Withers, P.J.A., and S.C. Jarvis. 1998. Mitigation options for diffuse phosphorus loss to water. Soil Use Manage. 14:186-192.

Yoon, S.H., I.J. Kang, and C.H. Lee. 1999. Fouling of inorganic membrane and flux enhancement in membrane-coupled anaerobic bioreactor. Separation Sci. Technol. 34(5):709-724.

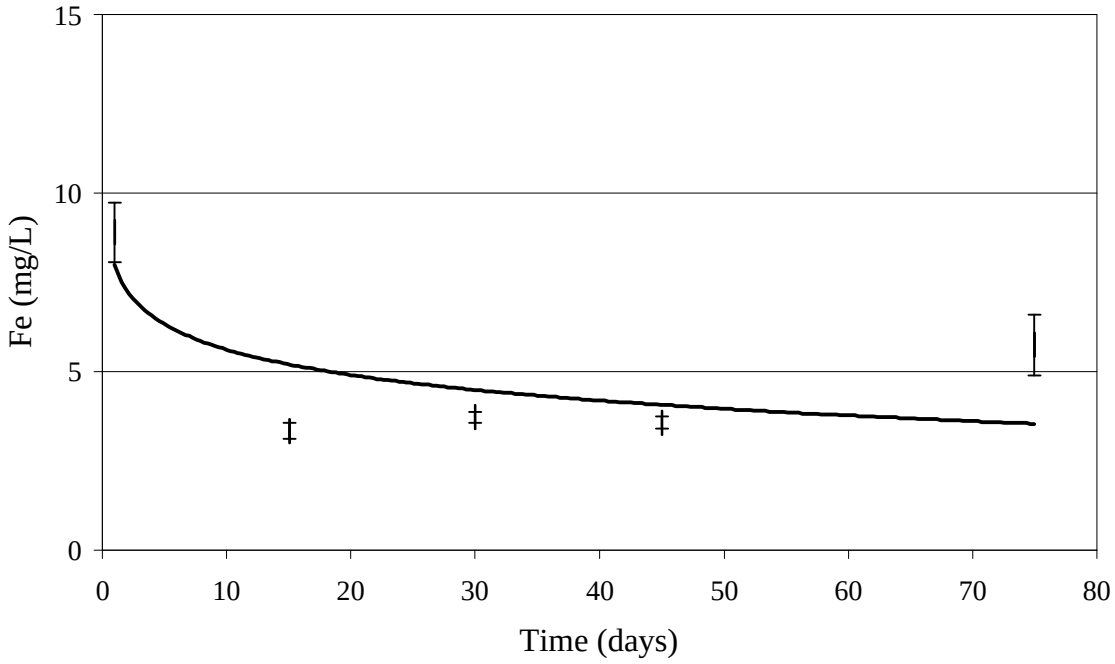
Zhang, X., S.E. Feagley, J.W. Day, W.H. Conner, I.D. Hesse, J.M. Rybczyk, and W.H. Hudnall. 2000. A water chemistry assessment of wastewater remediation in a natural swamp. J. Environ. Qual. 29:1960-1968.

APPENDIX A

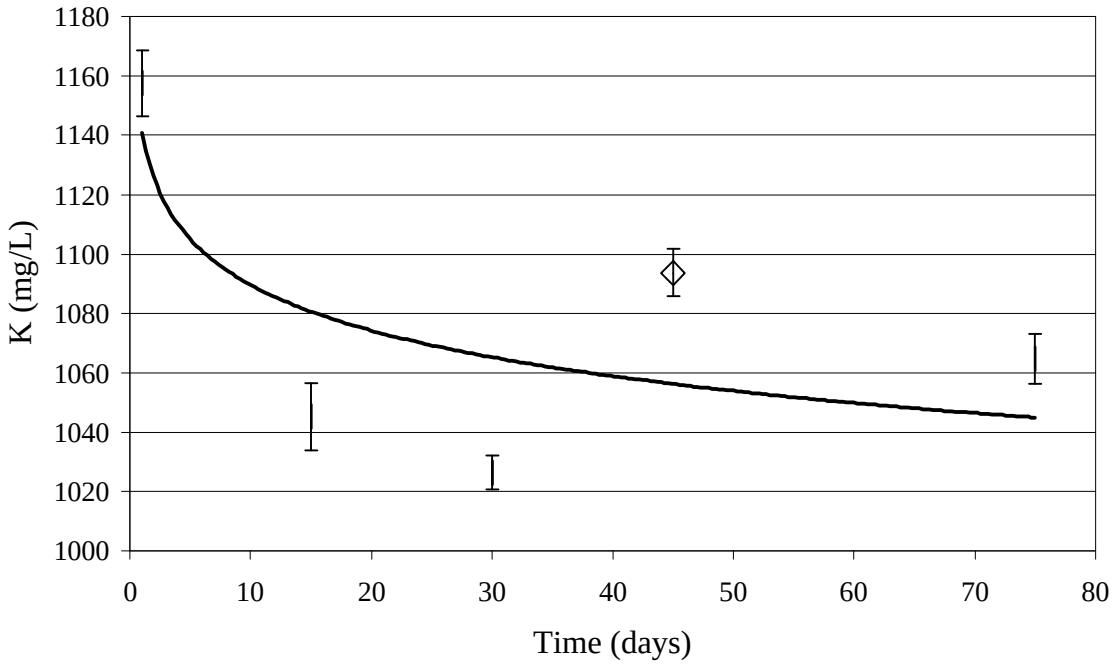
EFFECT OF SETTLING



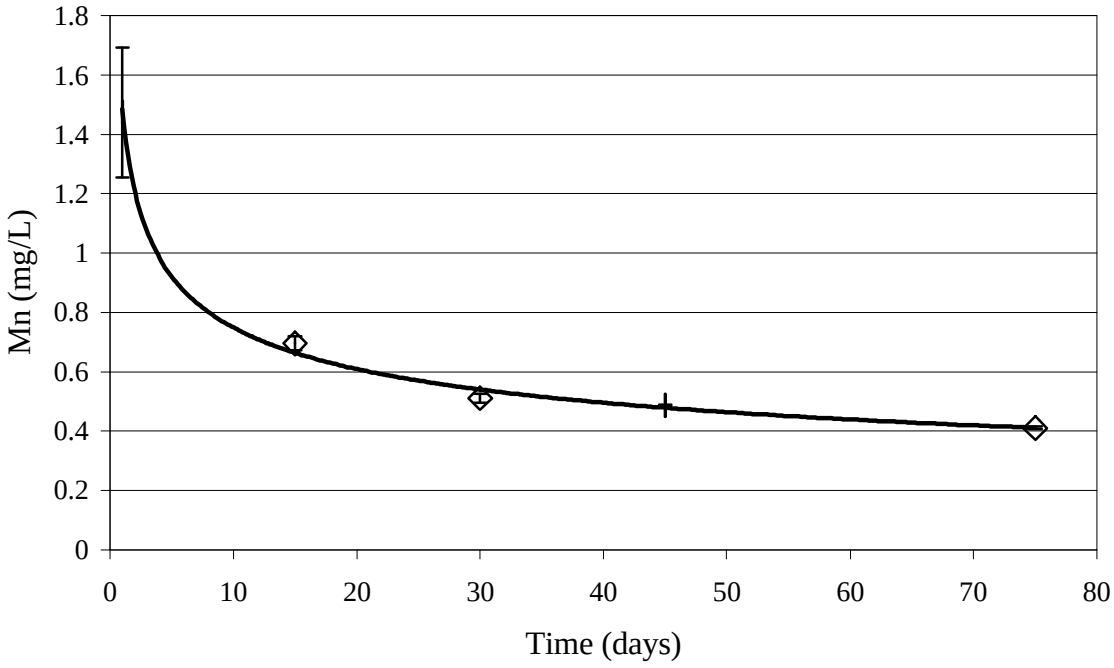
A 1: Changes in effluent Cu concentrations with settling time.



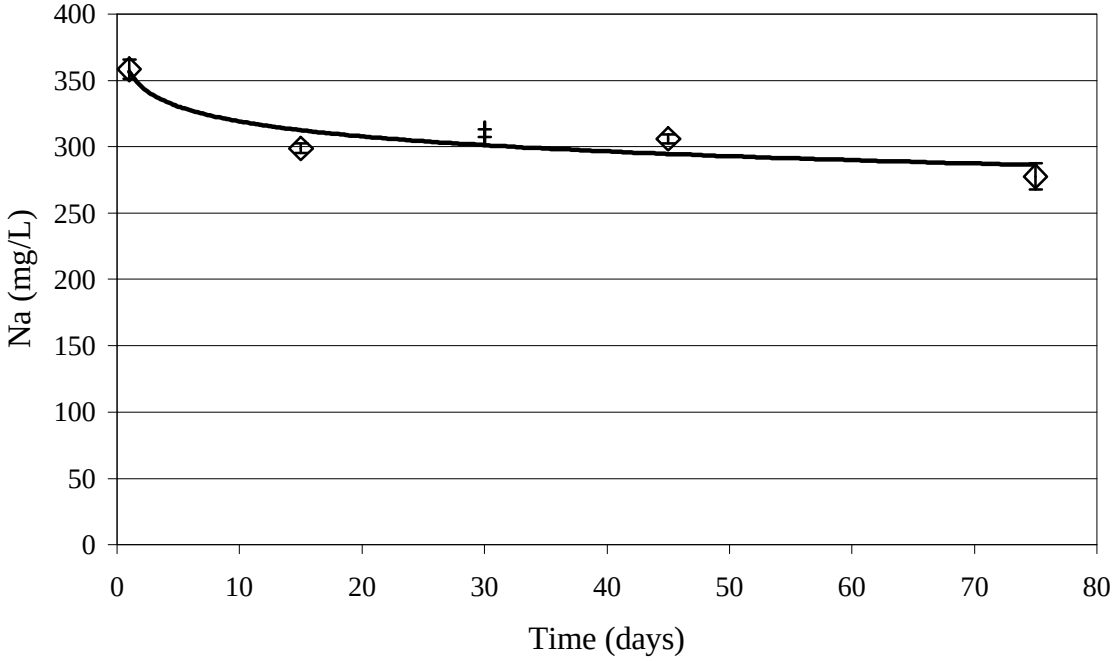
A 2: Changes in Fe concentration in the effluent with settling time.



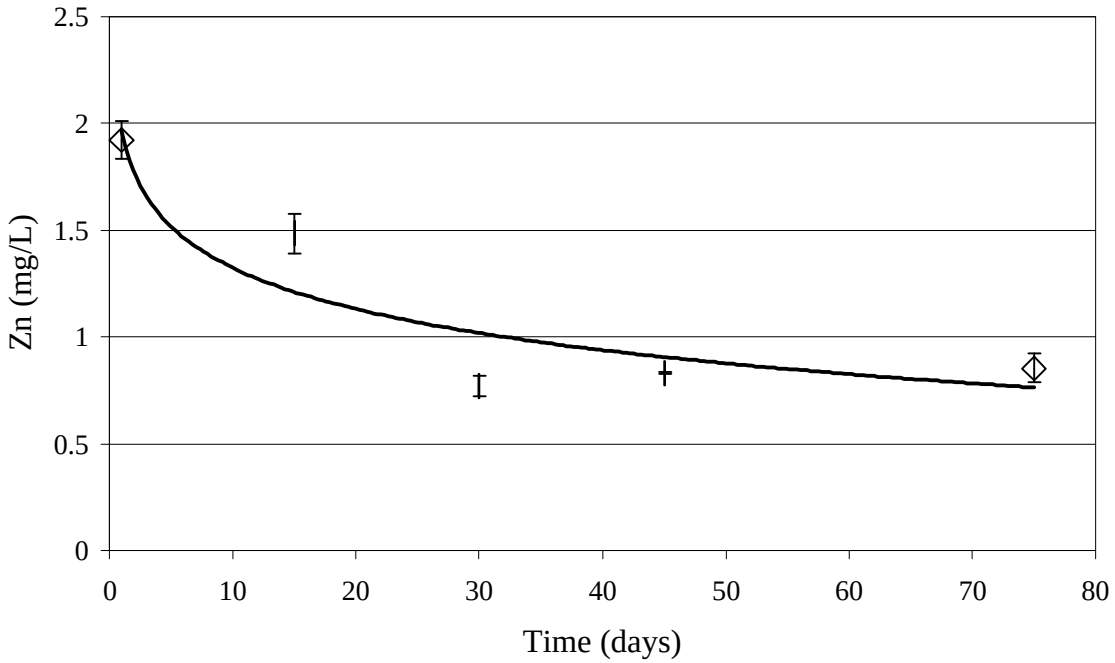
A 3: Changes in solution K concentration with time.



A 4: Changes in Mn concentration in the effluent with increasing time.



A 5: Sodium concentration in the solution changes with time.



A 6: Changes in solution zinc concentration as time passes.

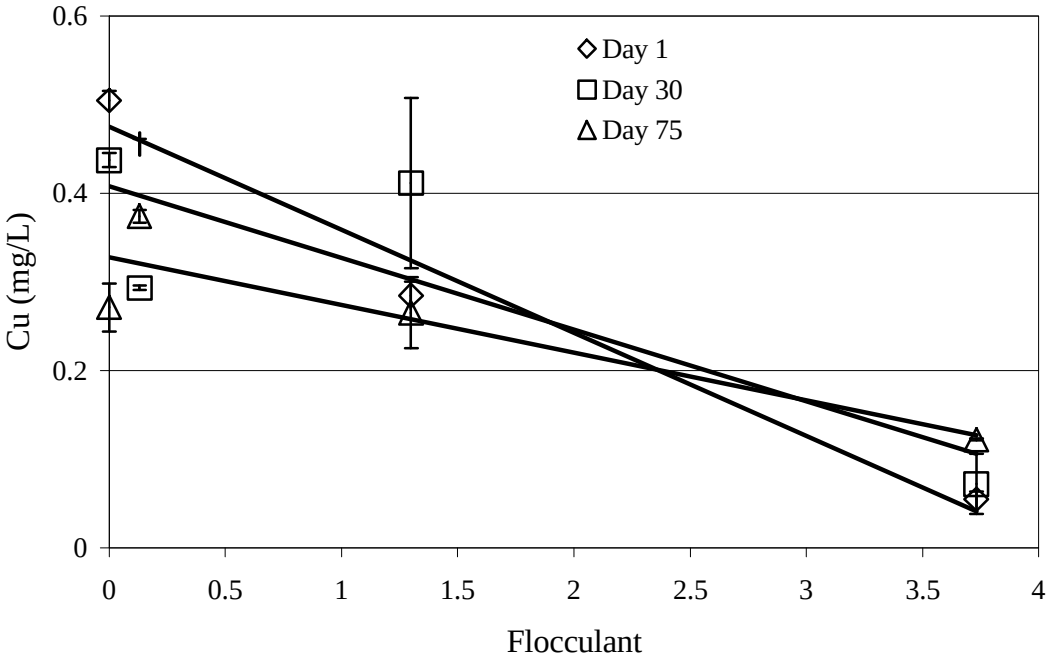
Table 7: Changes in average N, Ca, Mg, K, P, Zn, Mn, Cu, Fe, and Na concentrations as a function of settling time. Confidence intervals are for α=0.05.

Flocculant ($mg\ L^{-1}$)	Time (days)	N ($mg\ L^{-1}$)	Ca ($mg\ L^{-1}$)	Mg ($mg\ L^{-1}$)	K ($mg\ L^{-1}$)	P ($mg\ L^{-1}$)	Zn ($mg\ L^{-1}$)
0	1	660±3	350±14	235±1	1158±11	75.667±1.621	1.923±0.088
0	15	680±6	266±9	182±2	1045±11	38.733±0.024	1.484±0.094
0	30	633±4	217±11	184±1	1026±6	27.000±0.015	0.769±0.048
0	45	688±3	274±4	187±1	1094±8	24.293±0.003	0.831±0.005
0	75	631±1	242±2	182±2	1065±8	20.627±0.004	0.854±0.068

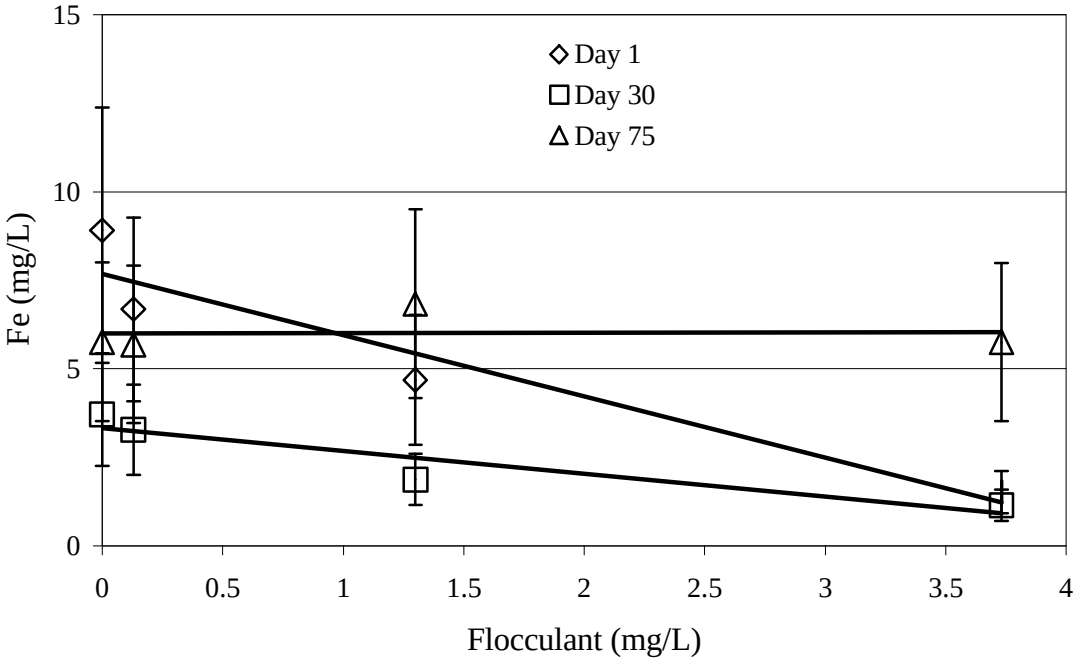
Flocculant ($mg\ L^{-1}$)	Time (days)	Mn ($mg\ L^{-1}$)	Cu ($mg\ L^{-1}$)	Fe ($mg\ L^{-1}$)	Na ($mg\ L^{-1}$)
0	1	1.475±0.218	0.505±0.011	8.910±3.470	358±7
0	15	0.696±0.024	0.305±0.007	3.333±1.298	299±4
0	30	0.511±0.015	0.437±0.008	3.717±1.447	310±3
0	45	0.487±0.003	0.270±0.001	3.567±1.389	306±3
0	75	0.411±0.004	0.271±0.027	5.755±2.241	278±10

APPENDIX B

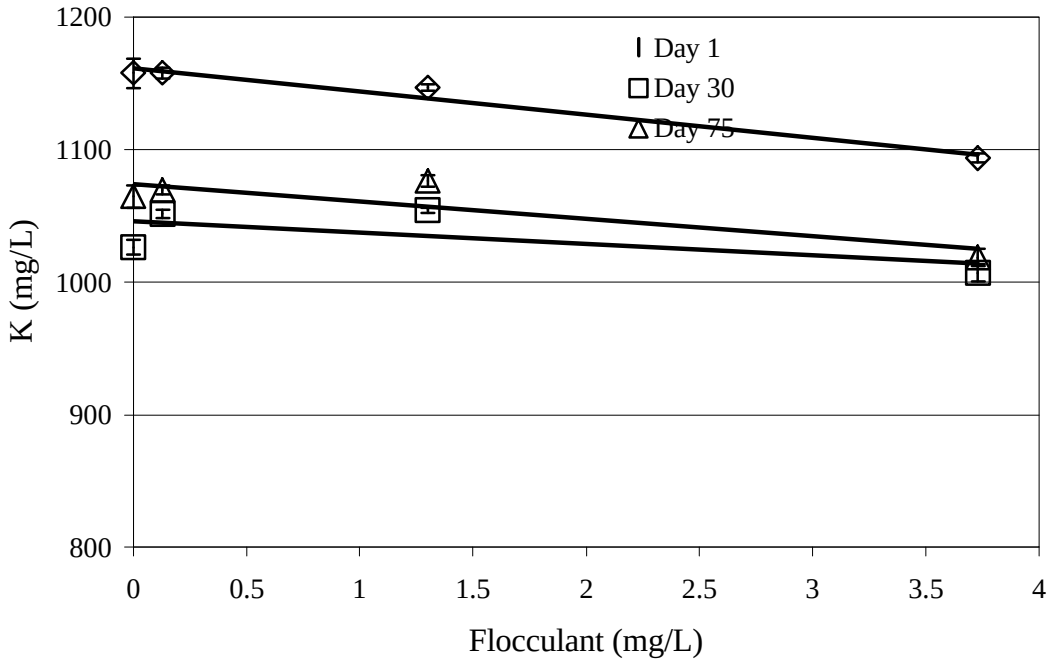
FLOCCULATION



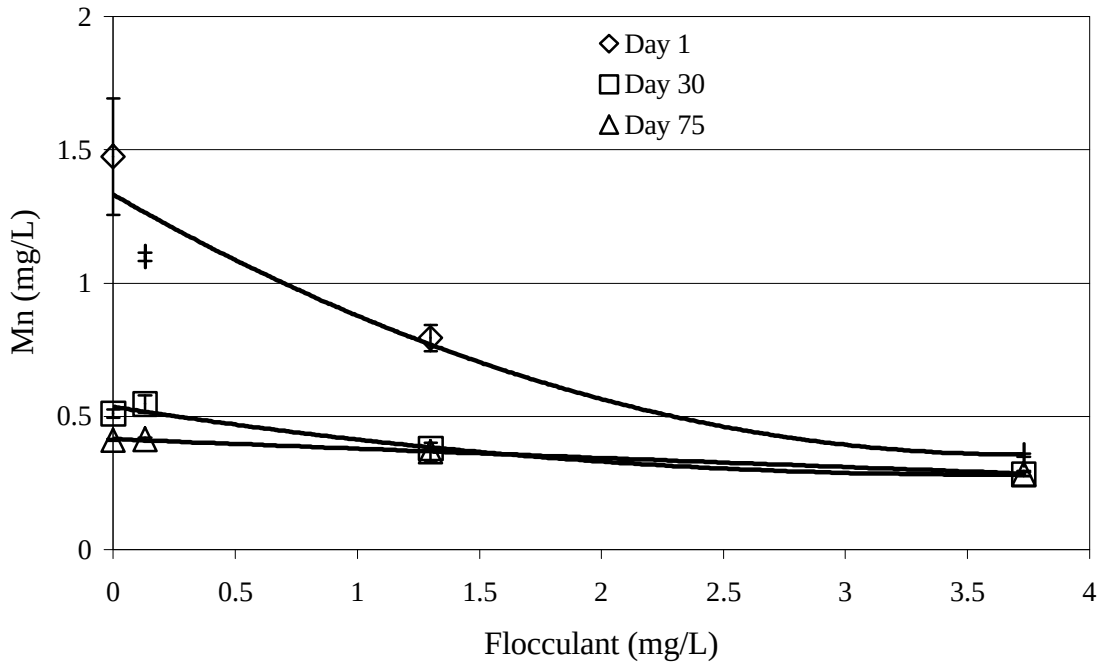
B 1: Changes in Cu in the solution as flocculant increases.



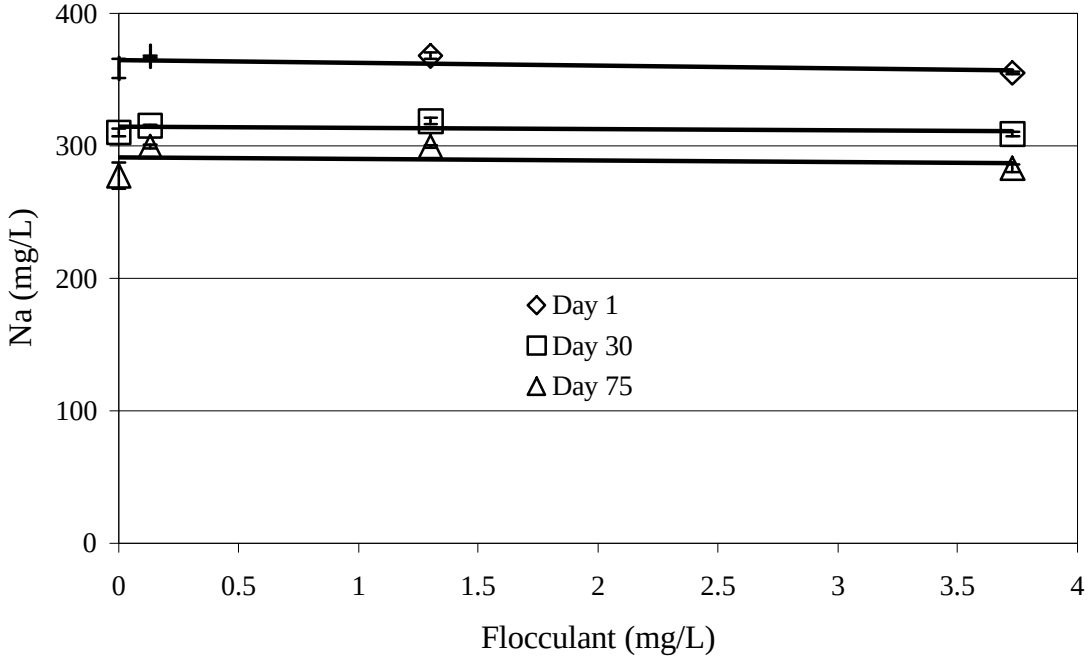
B 2: Changes in solution Fe with increasing flocculant.



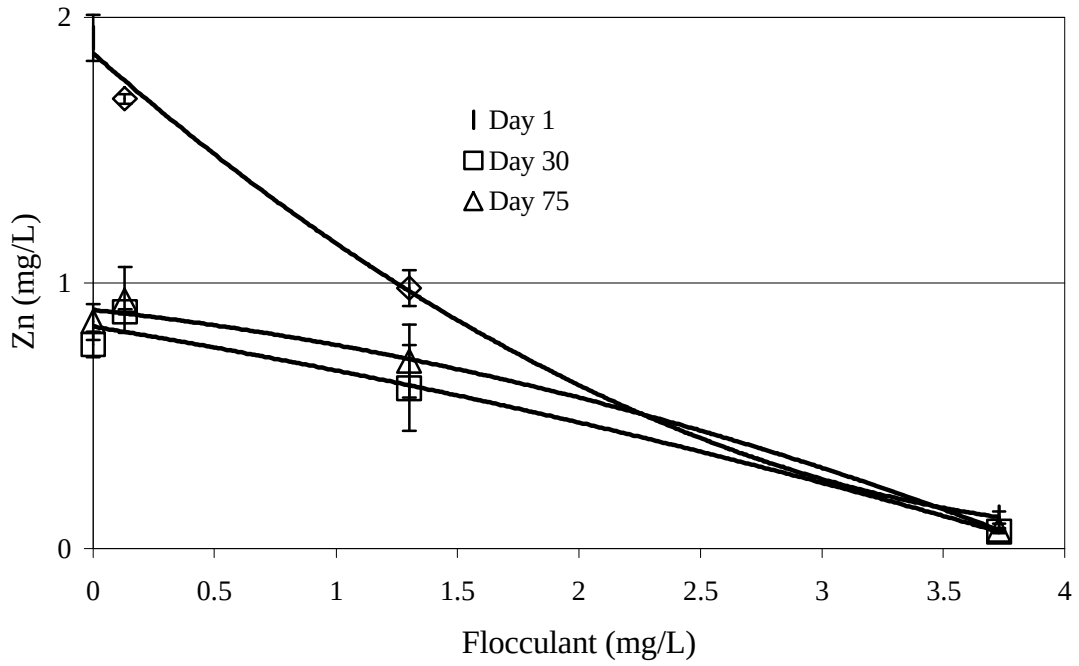
B 3: The effect of increasing flocculant on K concentration in the solution.



B 4: Manganese changes in the solution with increasing flocculant.



B 5: Changes in solution sodium concentration as flocculant increases.



B 6: Changes in zinc concentration in the solution with increasing flocculant.

Table 8: Average N, Ca, Mg, K, P, and Zn concentrations with flocculant concentration and time (days).

Flocculant ($mg\ L^{-1}$)	Time (days)	N ($mg\ L^{-1}$)	Ca ($mg\ L^{-1}$)	Mg ($mg\ L^{-1}$)	K ($mg\ L^{-1}$)	P ($mg\ L^{-1}$)	Zn ($mg\ L^{-1}$)
0	1	660±3	350±14	235±1	1158±11	75.667±1.621	1.923±0.088
0.13	1	642±3	341±3	235±1	1158±4	69.333±0.450	1.693±0.018
0.42	1	662±2	371±3	235±3	1156±10	67.333±1.124	1.763±0.082
1.3	1	596±8	304±12	225±0	1147±2	47.667±2.504	0.980±0.068
3.73	1	492±2	260±4	215±1	1094±3	26.333±0.980	0.117±0.023
0	15	680±6	266±9	182±2	1045±11	38.733±0.024	1.484±0.094
0.13	15	654±2	263±2	180±2	1031±15	36.800±0.001	1.501±0.074
0.42	15	629±4	278±10	186±2	1086±3	34.967±0.040	1.153±0.036
1.3	15	596±1	282±1	191±0	1087±5	31.900±0.014	0.737±0.006
3.73	15	529±3	253±1	184±1	1023±4	29.800±0.004	0.250±0.016
0	30	633±4	217±11	184±1	1026±6	27.000±0.015	0.769±0.048
0.13	30	635±4	250±28	189±2	1052±3	22.667±0.032	0.892±0.009
0.42	30	645±12	274±11	188±2	1047±6	24.000±0.009	0.837±0.046
1.3	30	604±9	274±4	187±1	1054±2	18.667±0.003	0.603±0.161
3.73	30	548±5	260±3	182±2	1007±7	15.667±0.006	0.064±0.005
0	45	688±3	274±4	187±1	1094±8	24.293±0.003	0.831±0.005
0.13	45	695±0	272±2	187±0	1093±2	24.633±0.005	0.786±0.011
0.42	45	671±3	260±6	188±0	1106±1	20.823±0.004	0.620±0.003
1.3	45	632±3	228±0	180±2	1089±5	11.720±0.074	0.221±0.009
3.73	45	585±0	222±3	177±1	1037±2	14.223±0.001	0.081±0.006
0	75	631±1	242±2	182±2	1065±8	20.627±0.004	0.854±0.068
0.13	75	627±0	232±1	182±1	1070±3	21.093±0.006	0.935±0.124
0.42	75	636±6	220±6	178±1	1066±6	18.757±0.015	0.939±0.131
1.3	75	600±5	229±12	179±1	1076±4	15.220±0.033	0.706±0.138
3.73	75	577±3	205±9	174±2	1019±6	15.880±0.010	0.070±0.006

Table 9: Average Cu, Fe, Mn, Na, and P concentrations with changes in time (days) and flocculant concentration.

Flocculant (mg L^{-1})	Time (days)	Cu (mg L^{-1})	Fe (mg L^{-1})	Mn (mg L^{-1})	Na (mg L^{-1})	P (mg L^{-1})
0	1	0.505±0.011	8.910±3.470	1.475±0.218	358±7	75.667±1.621
0.13	1	0.456±0.006	6.680±2.601	1.100±0.016	368±1	69.333±0.450
0.42	1	0.453±0.007	7.027±2.736	1.219±0.010	367±3	67.333±1.124
1.3	1	0.285±0.016	4.683±1.824	0.794±0.048	368±3	47.667±2.504
3.73	1	0.055±0.009	1.513±0.589	0.354±0.006	355±1	26.333±0.980
0	15	0.305±0.007	3.333±1.298	0.696±0.024	299±4	38.733±0.024
0.13	15	0.301±0.004	3.000±1.168	0.645±0.001	298±5	36.800±0.001
0.42	15	0.254±0.009	3.667±1.428	0.659±0.040	313±1	34.967±0.040
1.3	15	0.140±0.003	6.000±2.337	0.559±0.014	319±1	31.900±0.014
3.73	15	0.015±0.002	0.000±0.000	0.364±0.004	299±2	29.800±0.004
0	30	0.437±0.008	3.717±1.447	0.511±0.015	310±3	27.000±0.015
0.13	30	0.293±0.003	3.273±1.275	0.546±0.032	315±1	22.667±0.032
0.42	30	0.223±0.005	2.757±1.073	0.517±0.009	313±2	24.000±0.009
1.3	30	0.411±0.096	1.873±0.730	0.380±0.003	319±2	18.667±0.003
3.73	30	0.072±0.034	1.140±0.444	0.283±0.006	309±2	15.667±0.006
0	45	0.270±0.001	3.567±1.389	0.487±0.003	306±3	24.293±0.003
0.13	45	0.267±0.006	3.216±1.252	0.476±0.005	312±2	24.633±0.005
0.42	45	0.206±0.000	2.432±0.947	0.414±0.004	314±1	20.823±0.004
1.3	45	0.066±0.001	1.752±0.682	0.359±0.074	306±2	11.720±0.074
3.73	45	0.024±0.001	1.232±0.480	0.213±0.001	298±2	14.223±0.001
0	75	0.271±0.027	5.755±2.241	0.411±0.004	278±10	20.627±0.004
0.13	75	0.374±0.007	5.688±2.215	0.414±0.006	299±1	21.093±0.006
0.42	75	0.301±0.005	5.430±2.114	0.402±0.015	295±1	18.757±0.015
1.3	75	0.265±0.040	6.833±2.661	0.368±0.033	299±1	15.220±0.033
3.73	75	0.122±0.001	5.746±2.238	0.286±0.010	283±3	15.880±0.010

APPENDIX C

PROPERTIES OF THE SOLIDS

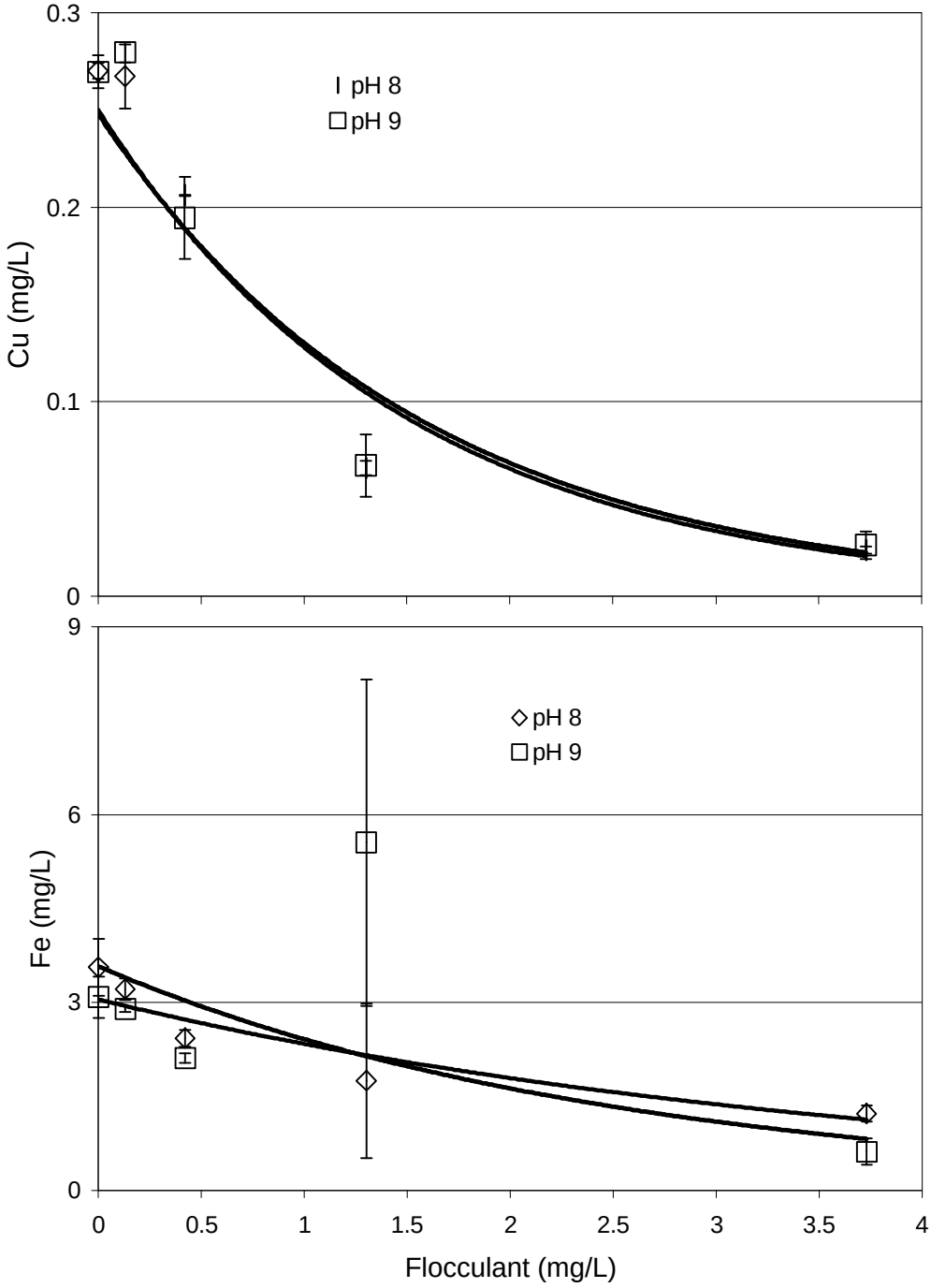
Table 10: Differences between the untreated and flocculated solids.

	Units	Flocculated	Amount removed from 190 L* (mg)	Untreated	Amount removed from 190L* (mg)
Total recovered	$g*190\ L^{-1}$	834	-	585	-
TKN	$mg\ kg^{-1}$	24153	20144	26879	15724
Ca	$mg\ kg^{-1}$	39369	32834	45733	26754
Cu	$mg\ kg^{-1}$	82	68	98	57
Fe	$mg\ kg^{-1}$	328	274	335	196
K	$mg\ kg^{-1}$	20107	16769	21370	12501
Mg	$mg\ kg^{-1}$	13498	11257	14110	8254
Mn	$mg\ kg^{-1}$	340	284	460	269
Na	$mg\ kg^{-1}$	5759	4803	6202	3628
P	$mg\ kg^{-1}$	17649	14719	20268	11857
Zn	$mg\ kg^{-1}$	432	360	539	315

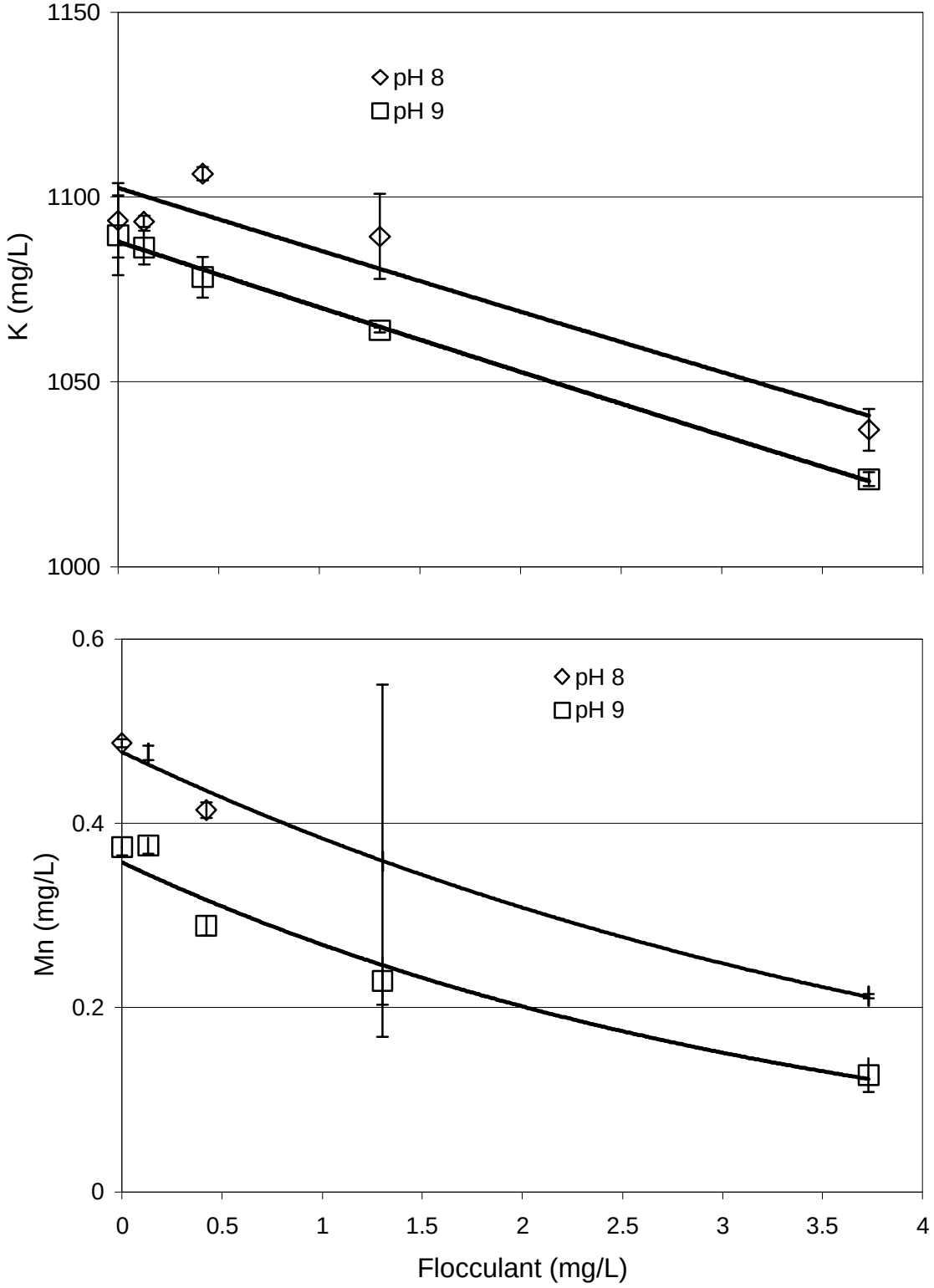
*Amount removed from 190L=
Weight of solids recovered from 190L (g/190L)XConcentration(mg/kg)/1000mg/g

APPENDIX D

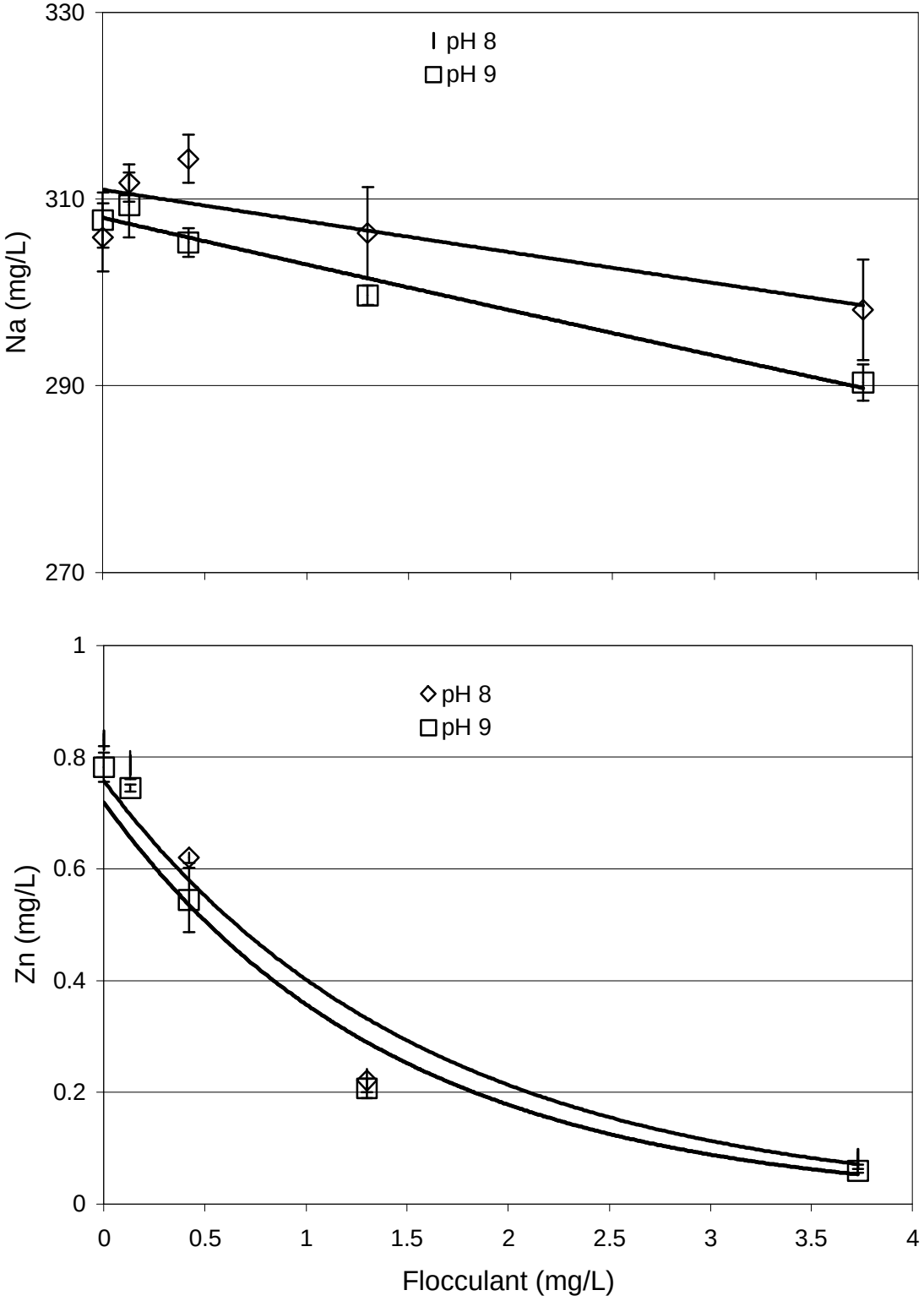
PRECIPITATION



D 1: Changes in Cu and Fe concentrations with pH and flocculant concentration.



D 2: Changes in solution K and Mn concentrations with pH and flocculant concentrations.



D 3: Changes in Na and Zn concentrations in the solution with pH and flocculant.

Table 11: Changes in TKN, Ca, Mg, K, and P concentrations with time and flocculant concentration.

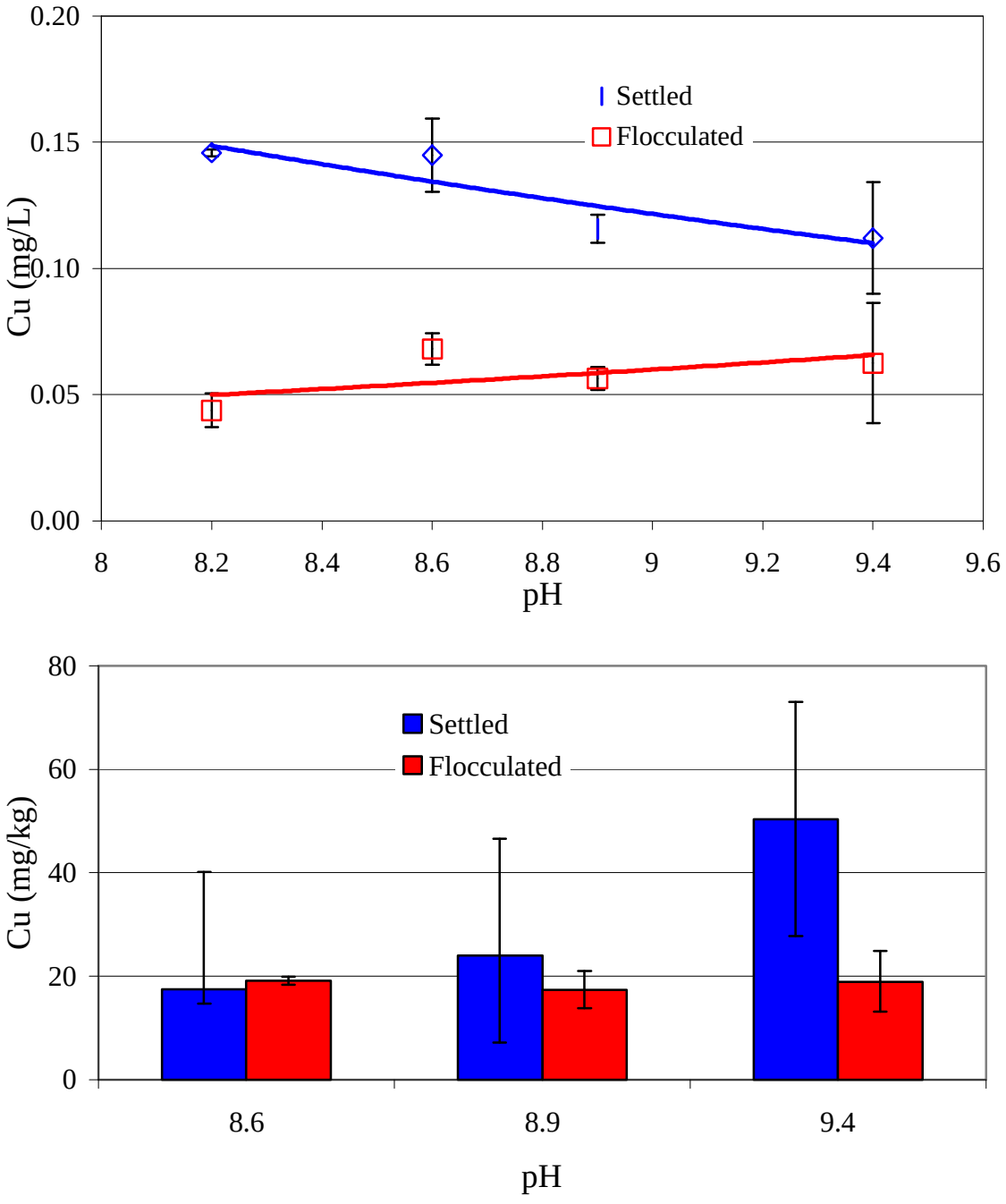
Flocculant mg L^{-1}	Time days	pH	Ca mg L^{-1}	Mg mg L^{-1}	P mg L^{-1}	K mg L^{-1}	TKN mg L^{-1}
0	30	9	217±24	189±0	25.54±1.45	1063±5	627±5
0.13	30	9	31±3	163±1	9.34±0.19	1022±10	1260±39
0.42	30	9	29±1	165±2	7.46±0.22	1024±6	1208±24
1.3	30	9	16±1	164±1	3.38±0.15	1022±3	1174±25
3.73	30	9	14±1	162±1	1.62±0.09	1004±4	1041±40
0	30	8.2	217±13	184±0	25.10±0.60	1026±7	633±10
0.13	30	8.2	250±28	189±4	27.17±2.98	1052±9	635±5
0.42	30	8.2	274±10	188±2	25.81±1.53	1047±12	645±15
1.3	30	8.2	274±8	187±1	18.34±0.39	1054±5	604±9
3.73	30	8.2	260±9	182±5	15.73±2.53	1007±14	548±5
0	45	9	93±8	174±2	12.43±0.30	1090±11	1196±16
0.13	45	9	94±12	174±2	12.39±0.08	1086±5	1169±15
0.42	45	9	56±5	171±0	9.45±0.38	1078±5	1174±6
1.3	45	9	26±2	167±2	3.50±0.69	1064±1	1106±30
3.73	45	9	15±1	160±0	1.74±0.13	1024±2	1072±13
0	45	8.2	274±11	187±2	24.29±1.05	1094±10	688±7
0.13	45	8.2	272±3	187±1	24.63±0.72	1093±2	695±0
0.42	45	8.2	260±16	188±1	20.82±1.07	1106±2	671±7
1.3	45	8.2	228±1	180±4	11.72±0.27	1089±12	632±7
3.73	45	8.2	222±7	177±2	14.22±0.54	1037±6	585±0
0	75	9	77±5	172±1	12.03±0.25	1052±15	899±4
0.13	75	9	70±4	165±1	11.21±0.20	1016±1	893±12
0.42	75	9	90±10	170±1	10.02±0.29	1057±3	916±6
1.3	75	9	31±4	167±0	4.10±0.61	1035±7	881±23
3.73	75	9	35±22	155±4	1.61±0.07	987±11	822±4
0	75	8.2	242±6	182±1	20.63±0.65	1065±9	631±1
0.13	75	8.2	232±1	182±1	21.09±1.45	1070±4	627±0
0.42	75	8.2	220±16	178±2	18.76±0.34	1066±13	636±16
1.3	75	8.2	229±28	179±2	15.22±0.86	1076±12	600±9
3.73	75	8.2	205±9	174±4	15.880±0.441	1019±9	577±3

Table 12: Changes in Cu, Fe, Mn, Na, and Zn concentrations with time and flocculant concentration.

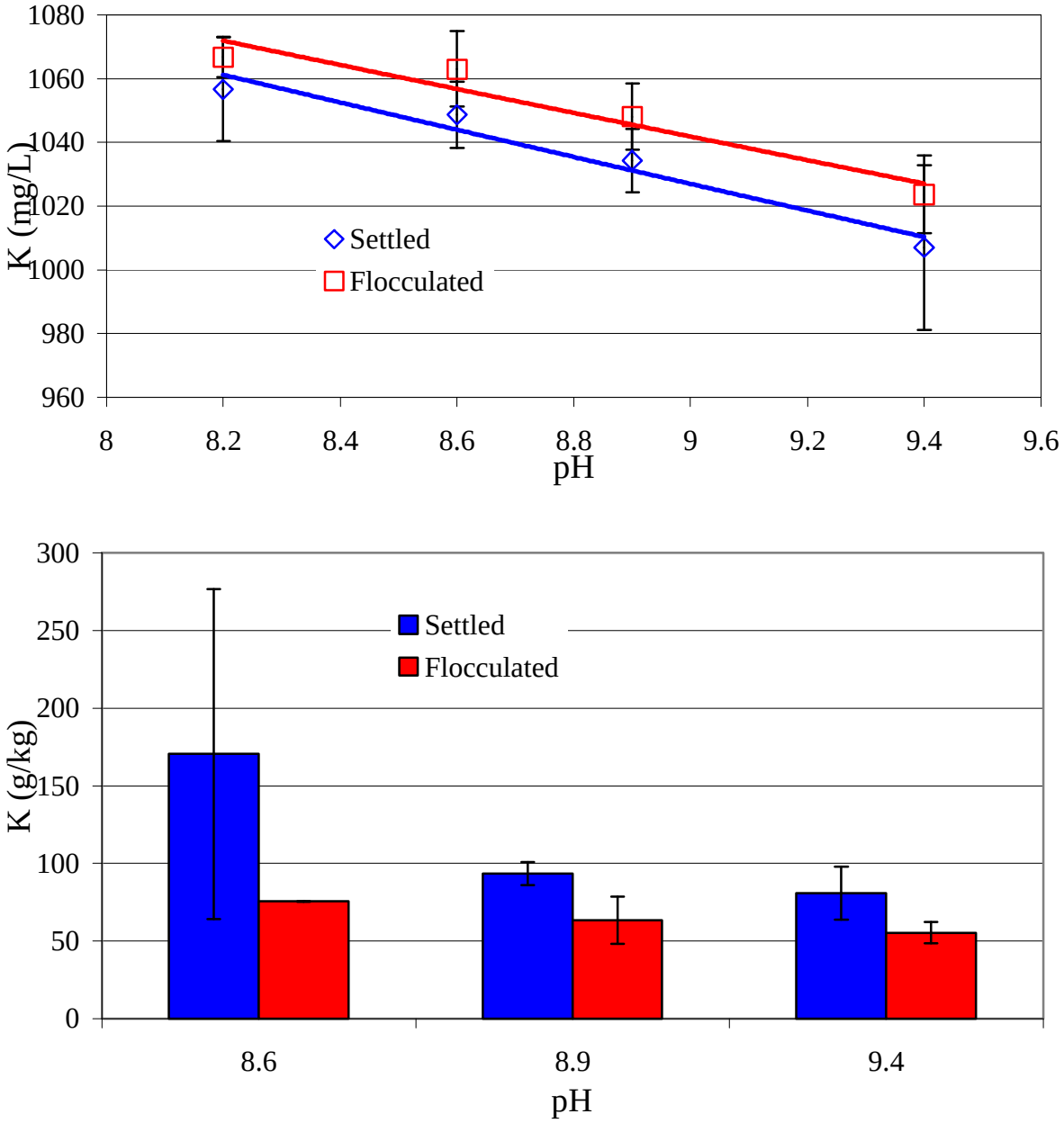
Flocculant	Time	pH	Cu	Fe	Mn	Na	Zn
mg L^{-1}	days		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
0	30	9	0.418±0.075	3.963±0.515	0.554±0.024	323±3	0.971±0.007
0.13	30	9	0.219±0.009	2.791±0.505	0.349±0.009	306±5	0.714±0.064
0.42	30	9	0.171±0.011	2.215±0.281	0.307±0.007	311±5	0.535±0.031
1.3	30	9	0.114±0.071	1.354±0.099	0.191±0.008	308±2	0.186±0.012
3.73	30	9	0.191±0.012	0.956±0.202	0.144±0.006	312±2	0.079±0.011
0	30	8.2	0.437±0.023	3.717±0.402	0.511±0.026	310±3	0.905±0.033
0.13	30	8.2	0.293±0.007	3.273±0.026	0.546±0.036	315±1	0.892±0.023
0.42	30	8.2	0.223±0.011	2.754±0.252	0.517±0.010	313±5	0.701±0.018
1.3	30	8.2	0.411±0.227	1.872±0.244	0.379±0.009	319±7	0.603±0.381
3.73	30	8.2	0.072±0.086	1.139±0.297	0.283±0.018	309±4	0.063±0.012
0	45	9	0.270±0.008	3.089±0.333	0.374±0.009	308±3	0.782±0.026
0.13	45	9	0.280±0.005	2.902±0.053	0.376±0.009	309±3	0.745±0.006
0.42	45	9	0.195±0.021	2.118±0.076	0.289±0.011	305±2	0.544±0.058
1.3	45	9	0.067±0.016	5.560±2.606	0.229±0.026	300±1	0.207±0.018
3.73	45	9	0.026±0.007	0.620±0.207	0.127±0.018	290±2	0.059±0.004
0	45	8.2	0.270±0.004	3.567±0.458	0.487±0.004	306±4	0.831±0.011
0.13	45	8.2	0.267±0.016	3.216±0.170	0.476±0.008	312±2	0.786±0.025
0.42	45	8.2	0.206±0.000	2.432±0.132	0.414±0.008	314±3	0.620±0.009
1.3	45	8.2	0.066±0.004	1.752±1.240	0.359±0.191	306±5	0.221±0.021
3.73	45	8.2	0.024±0.002	1.232±0.129	0.213±0.002	298±5	0.081±0.011
0	75	9	0.401±0.026	5.929±1.416	0.362±0.029	298±3	1.050±0.301
0.13	75	9	0.400±0.016	5.715±1.884	0.341±0.021	288±3	0.811±0.119
0.42	75	9	0.328±0.010	6.283±1.334	0.354±0.027	294±2	0.524±0.021
1.3	75	9	0.199±0.010	6.523±0.903	0.208±0.009	290±2	0.160±0.012
3.73	75	9	0.140±0.013	6.669±1.655	0.208±0.063	277±4	0.058±0.004
0	75	8.2	0.271±0.077	5.755±2.464	0.411±0.004	278±23	0.854±0.070
0.13	75	8.2	0.374±0.018	5.688±0.722	0.414±0.006	299±1	0.935±0.241
0.42	75	8.2	0.301±0.007	5.430±1.118	0.402±0.043	295±4	0.939±0.148
1.3	75	8.2	0.265±0.104	6.833±1.303	0.368±0.058	299±2	0.706±0.341
3.73	75	8.2	0.122±0.003	5.746±2.552	0.286±0.024	283±3	0.070±0.019

APPENDIX E

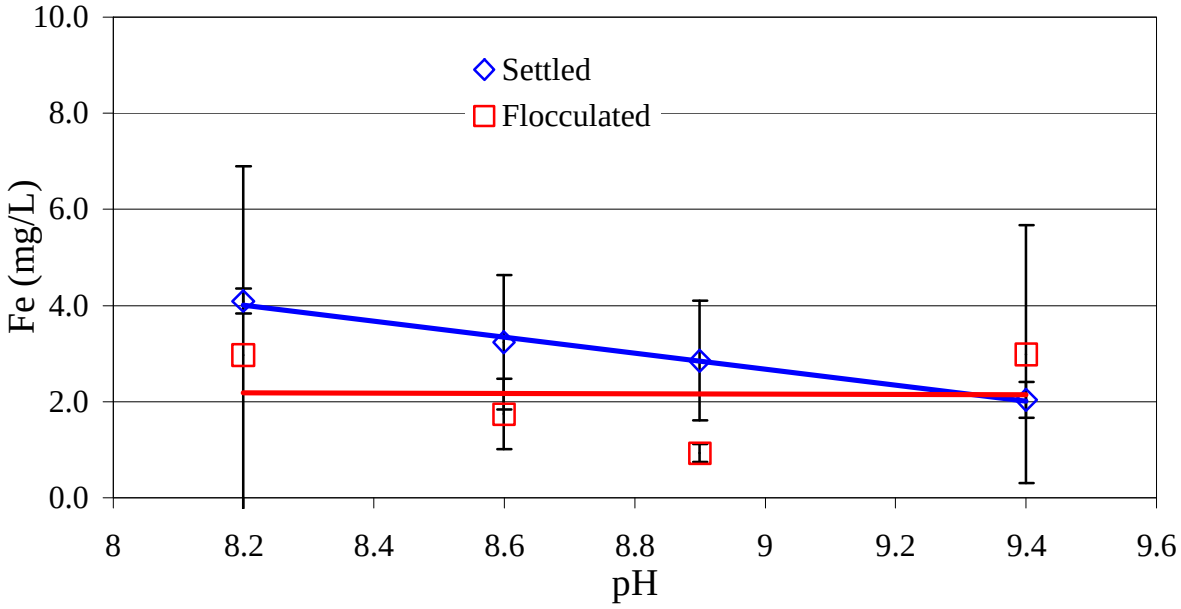
CHARACTERIZATION OF THE PRECIPITATES

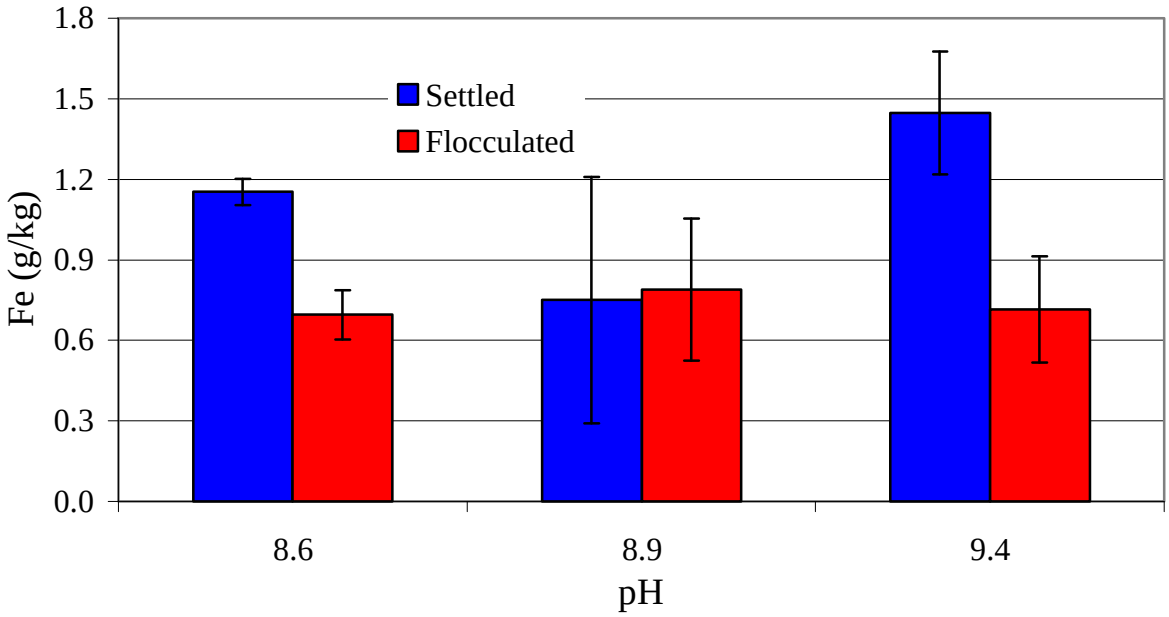


E 1: Solution (mg L^{-1}) and precipitate (mg L^{-1}) Cu as pH changes.

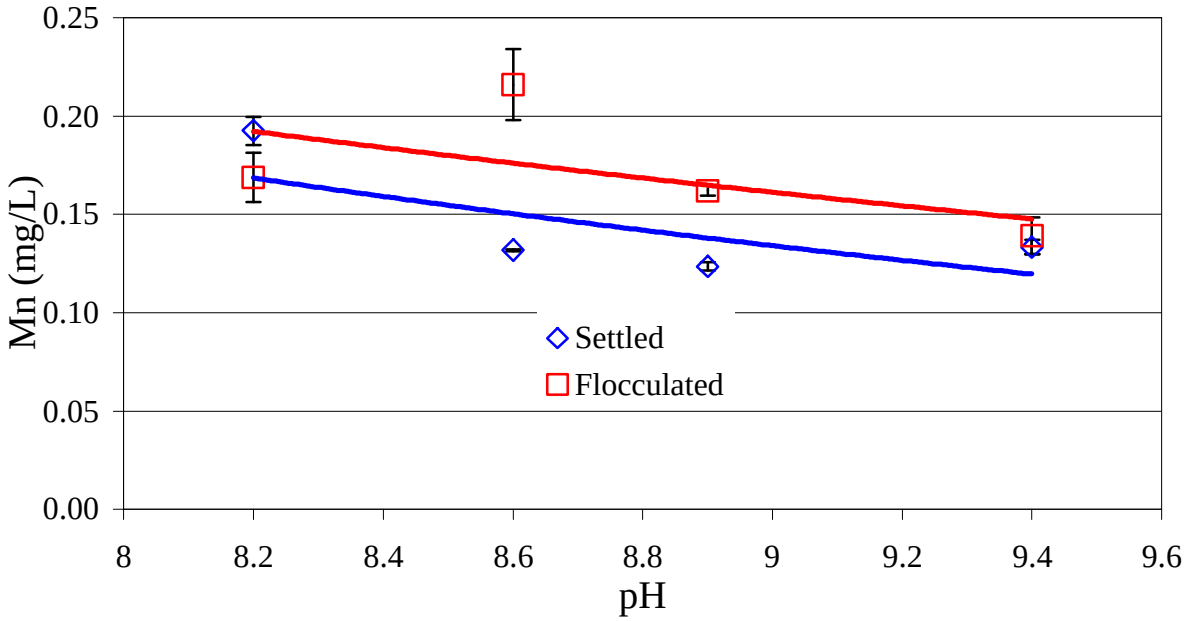


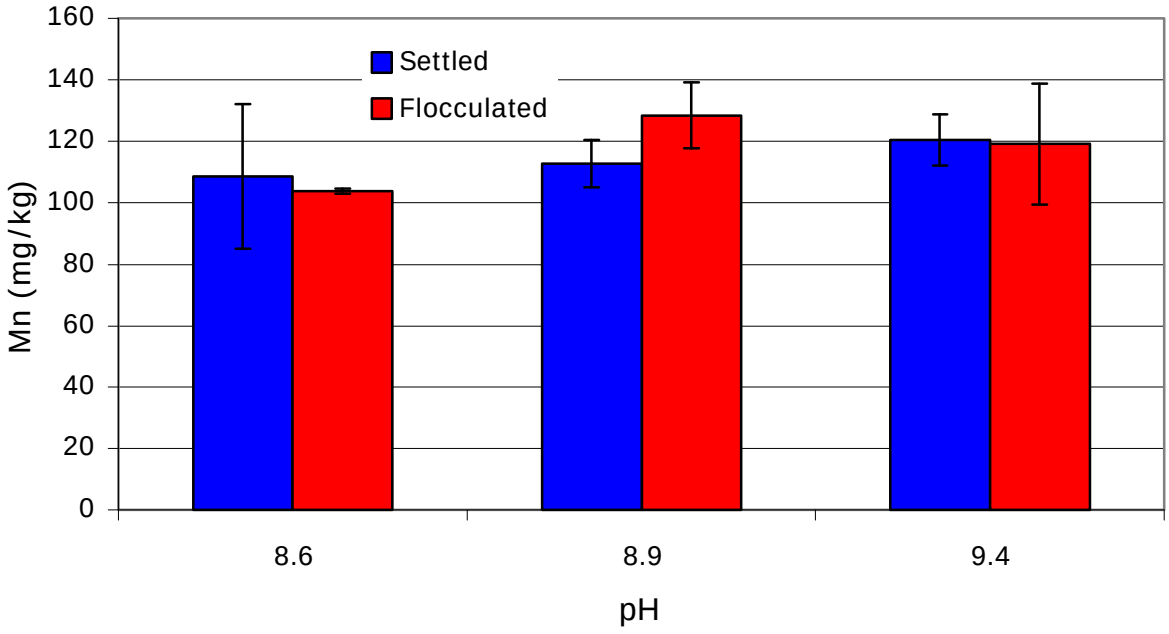
E 2: Potassium in the solution (mg L^{-1}) and precipitate (g kg^{-1}) as pH changes.



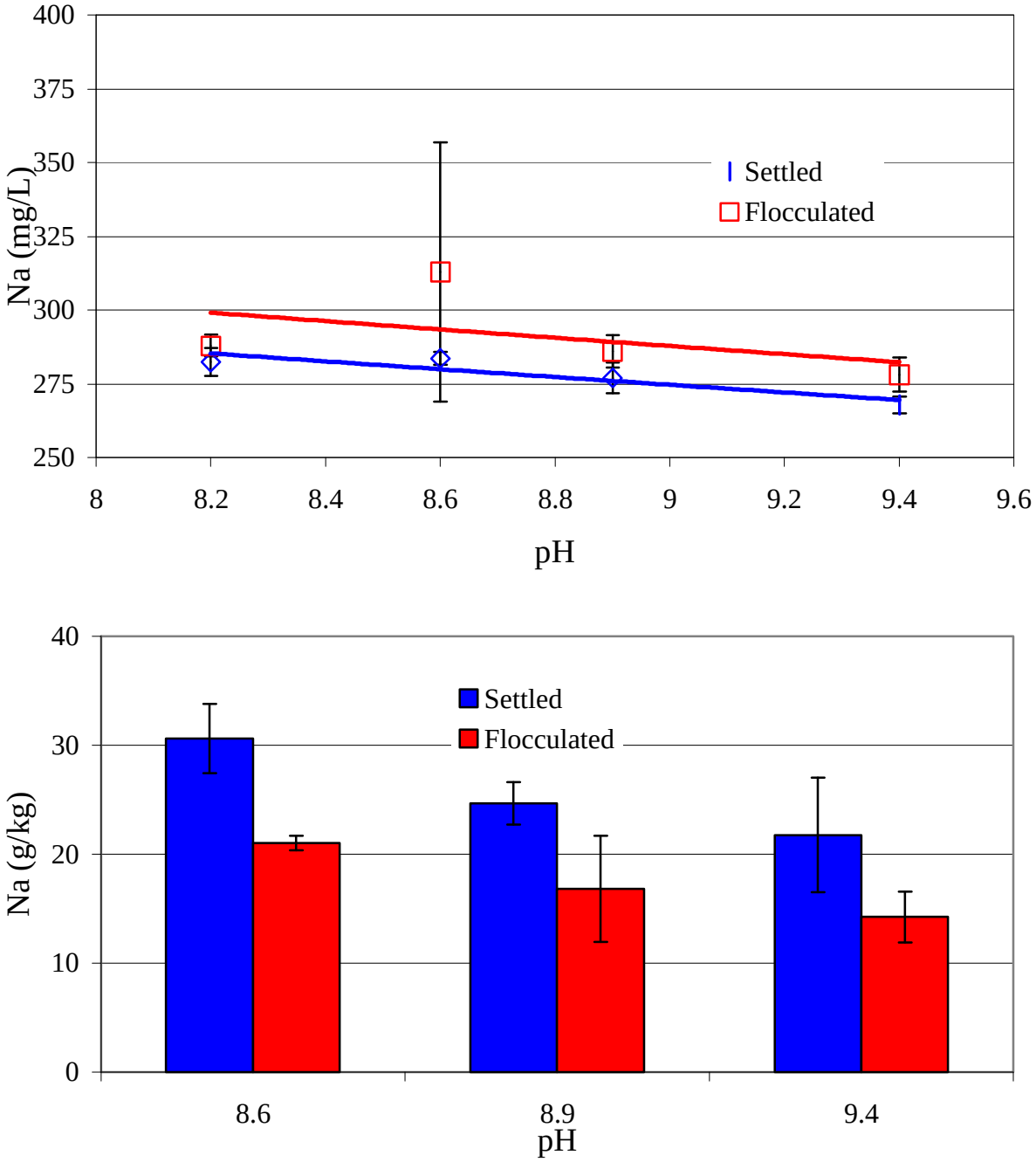


E 3: Iron in solution (mg L^{-1}) and precipitate (g kg^{-1}) as pH increases.

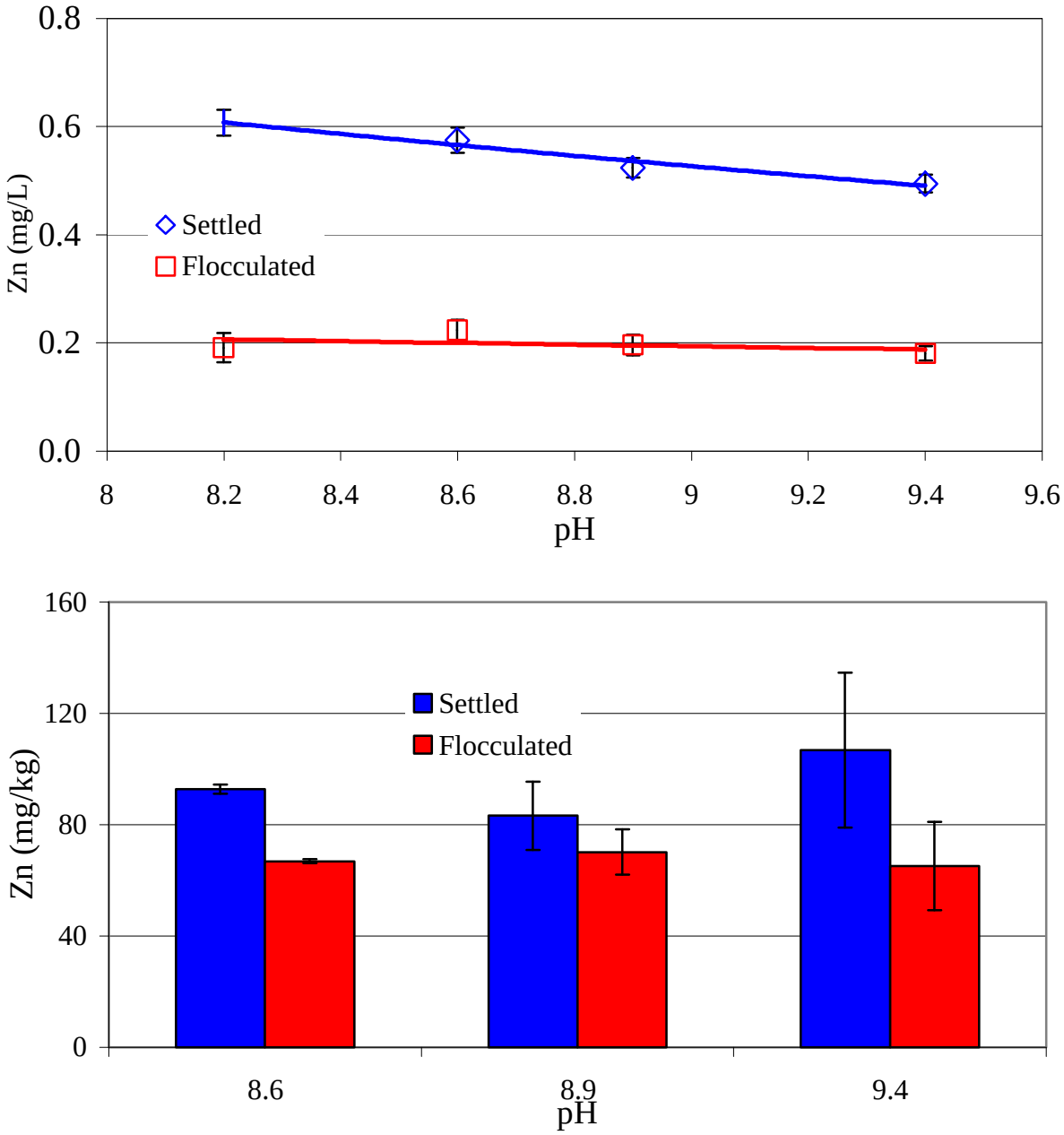




E 4: Solution (mg L^{-1}) and precipitate (mg kg^{-1}) manganese as pH changes.



E 5: Solution (mg L^{-1}) and precipitate (g kg^{-1}) sodium as pH changes.



E 6: Zinc in solution (mg L^{-1}) and precipitate (mg kg^{-1}) as pH increases.

Table 13: Concentrations of TKN, Ca, Mg, and P in the untreated and flocculated effluent.

	pH	TKN - Eff. mg L^{-1}	Ca - Eff. mg L^{-1}	K - Eff. mg L^{-1}	Mg - Eff. mg L^{-1}	P - Eff. mg L^{-1}
Untreated	8.2	651±11	189.2±71.7	1057±16	178±0.4	12.957±0.934
Untreated	8.6	765±13	42.4±0.4	1049±10	174±1.7	8.743±0.595
Untreated	8.9	773±99	28.0±3.2	1034±10	170.5±1.1	7.567±0.366
Untreated	9.4	1278±272	38.4±13.8	1007±26	165.7±3.5	7.587±0.729
Flocculated	8.2	467±13	75.8±82.8	1067±6	179.5±0.6	5.940±1.306
Flocculated	8.6	611±91	57.9±35.6	1063±12	176.5±3.1	5.971±1.464
Flocculated	8.9	874±142	23.5±6.4	1048±10	172.4±2.1	4.371±0.483
Flocculated	9.4	1530±12	11.4±1.1	1024±12	165.5±2.2	3.291±0.283

Table 14: Concentrations of TKN, Ca, Mg, and P in the precipitates from the untreated and flocculated effluents.

	pH	TKN - Prec. mg kg^{-1}	Ca - Prec. mg kg^{-1}	K - Prec. mg kg^{-1}	Mg - Prec. mg kg^{-1}	P - Prec. mg kg^{-1}
Untreated	8.2					
Untreated	8.6	10616±408	94493±25874	170510±106139	25956±506	7353±182
Untreated	8.9	9412±187	81127±8981	93488±7256	24621±1209	8636±1453
Untreated	9.4	8513±843	85861±6101	80882±17099	25459±1189	11257±599
Flocculated	8.2					
Flocculated	8.6	9878±51	83356±40373	75560±74	21011±856	7172±4363
Flocculated	8.9	9434±409	96098±53091	63387±15171	20525±1971	9330±3502
Flocculated	9.4	8886±783	110433±2148	55414±6166	20629±1310	11938±324

Table 15: Concentrations of Cu, Fe, Mn, Na, and Zn in the flocculated and untreated effluents.

	pH	Cu - Eff. mg L^{-1}	Fe - Eff. mg L^{-1}	Mn - Eff. mg L^{-1}	Na - Eff. mg L^{-1}	Zn - Eff. mg L^{-1}
Untreated	8.2	0.146±0.001	4.092±0.255	0.193±0.025	282±5	0.607±0.024
Untreated	8.6	0.145±0.015	3.239±1.401	0.132±0.001	284±2	0.575±0.023
Untreated	8.9	0.116±0.005	2.855±1.247	0.124±0.008	277±5	0.524±0.018
Untreated	9.4	0.112±0.022	2.043±0.382	0.133±0.012	268±3	0.494±0.016
Flocculated	8.2	0.044±0.007	2.978±3.930	0.169±0.042	288±4	0.191±0.027
Flocculated	8.6	0.068±0.006	1.747±0.735	0.216±0.061	313±44	0.223±0.020
Flocculated	8.9	0.056±0.005	0.934±0.190	0.162±0.009	286±5	0.196±0.019
Flocculated	9.4	0.062±0.024	2.991±2.682	0.139±0.032	278±6	0.180±0.013

Table 16: Concentrations of Cu, Fe, Mn, Na, and Zn in the precipitates from the flocculated and untreated effluents.

	pH	Cu - Prec. mg kg^{-1}	Fe - Prec. mg kg^{-1}	Mn - Prec. mg kg^{-1}	Na - Prec. mg kg^{-1}	Zn - Prec. mg kg^{-1}
Untreated	8.2					
Untreated	8.6	17.48±2.77	1154±43	108±24	30601±3185	92±2
Untreated	8.9	23.99±16.86	751±405	113±7	24649±1977	83±12
Untreated	9.4	50.36±22.60	1447±203	120±7	21756±5248	107±28
Flocculated	8.2					
Flocculated	8.6	19.10±0.75	696±81	104±1	21012±686	67±1
Flocculated	8.9	17.41±3.60	789±234	128±9	16814±4851	70±8
Flocculated	9.4	18.95±5.86	715±199	119±17	14213±2313	65±16

Table 17: XRD D-space matches for the precipitates from the flocculated effluent.

pH=8.6	pH=8.9	pH=9.4	Monohydro-calcite ($CaCO_3$*H20)	Struvite	Sylvite (KCl)	Halite (NaCl)	Ca Phospate ($Ca_3(PO_4)_2$)
5.59	5.61	5.59		5.61			
5.27	5.29	5.26	5.28				
4.30	4.33	4.31	4.32	4.26			
4.12	4.13	4.13		4.14			
3.27	3.30	3.28				3.26	
3.14	3.14	3.14			3.15		3.11
3.06	3.07	3.06	3.07 3.05				
2.93	2.95	2.94		2.92			
		2.90					2.89
2.82	2.83	2.82	2.82	2.80		2.82	
2.69	2.69	2.69		2.69			
2.65 2.55	2.66	2.65		2.67			2.62
			2.52				
2.49	2.50	2.49	2.49				
2.37	2.37	2.37	2.37				2.42
2.27	2.27	2.27	2.27				
2.22	2.23	2.22					2.21
2.16	2.17	2.16	2.16		2.22		
							2.08
2.04	2.09						2.04
1.99	2.00	2.00	1.99			1.99	2.01
1.93	1.93	1.93	1.94				1.94
			1.93				
1.81	1.82	1.82	1.82		1.82		
1.77	1.78	1.78	1.76				
1.76	1.77	1.76					1.73
1.73							1.73
1.71	1.71	1.71				1.70	
1.60	1.60	1.60				1.63	
1.57	1.57	1.57			1.57		1.56
1.53	1.53	1.53					1.52
1.49	1.50	1.49					1.52
1.44							1.44

Table 18: XRD D-space matches for the precipitates in the untreated effluent.

pH=8.6	pH=8.9	pH=9.4	Monohydro-calcite ($CaCO_3$*H20)	Struvite	Sylvite (KCl)	Halite (NaCl)	Ca-Phospate ($Ca_3(PO_4)_2$)
5.57				5.61			
5.26	5.26	5.23	5.28				
4.30	4.30	4.29	4.32	4.26			
	4.12			4.14			
		3.63					
		3.34					
	3.26	3.27				3.26	
3.14	3.13	3.13			3.15		3.11
3.06	3.05	3.05	3.07				
3.03	3.02	3.02	3.05				
2.94	2.93	2.93		2.92			
							2.89
2.82	2.82	2.81	2.82	2.80		2.82	
2.69				2.69			
2.63	2.64	2.64		2.67			2.62
	2.59						
			2.52				
2.49	2.48	2.48	2.49				
2.37	2.36	2.36	2.37				2.42
2.27	2.26	2.26	2.27				
2.22	2.22	2.22					2.21
2.16	2.16	2.16	2.16		2.22		
2.08	2.08	2.07					2.08
2.04	2.04	2.03					2.04
2.00	1.99	1.99	1.99			1.99	2.01
1.93	1.93	1.93	1.94				1.94
1.86		1.86	1.93				
1.81	1.81	1.81	1.82		1.82		
1.77	1.77	1.76	1.76				
1.76	1.76						1.73
1.72		1.71				1.70	
1.59	1.60	1.60				1.63	
1.57	1.57	1.57			1.57		
		1.56					1.56
1.53	1.53	1.52					1.52

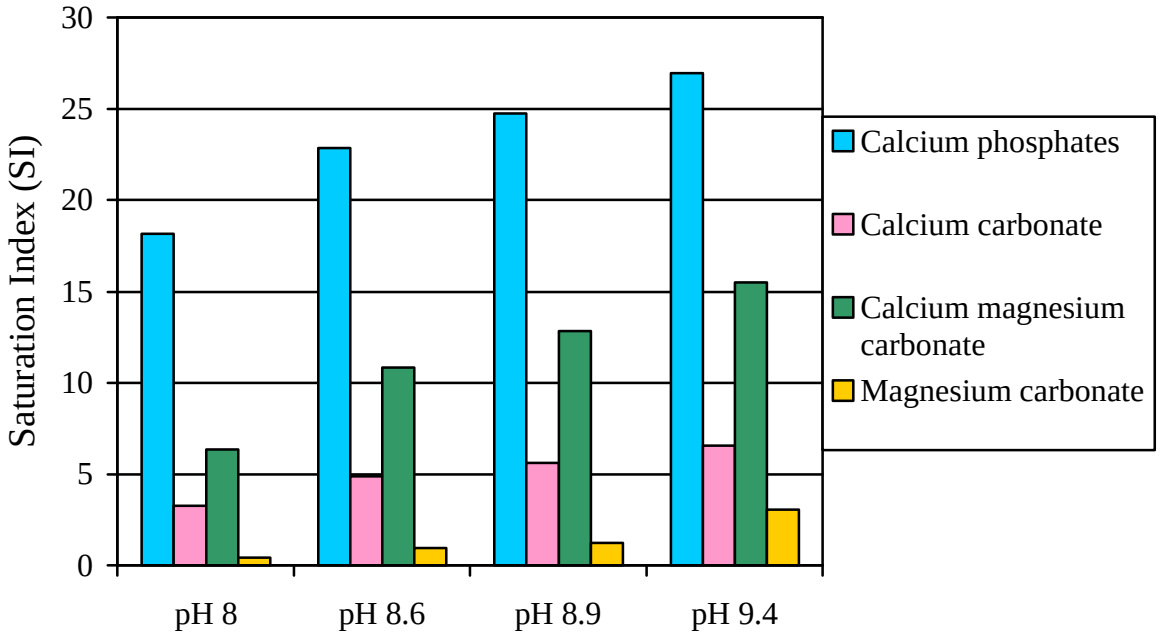
APPENDIX F

VISUAL MINTEQ

(Source: Royal Institute of Technology, 2003)

Input – Day 30 – Flocculated with 1.3 mg L^{-1} flocculant
* is based on an estimated value since carbonates were not measured

N	Ca	Mg	K	PO_4^{-3}	Na	CO_3^{-2}
mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
604	274	188	1100	82	308	500*



F 1: Saturation indexes of general species anticipated to precipitate based on Visual MINTEQ (Royal Institute for Technology, 2003). Calcium phosphates include: $Ca_3(PO_4)_2$ Beta; $Ca_4H(PO_4)_3*3H_2O$; $CaHPO_4$, and hydroxyapatite. Calcium carbonates include: aragonite and vaterite. Calcium and magnesium carbonates include: dolomite and huntite. Magnesium carbonates include: magnesite; hydromagnesite; and artinite. No magnesium phosphates were indicated as oversaturated.

APPENDIX G

GLOSSARY (SMITH AND SCOTT, 2002)

AAO process – This is an activated sludge process capable of achieving nitrification, denitrification, biological phosphorus removal, reduction of biochemical oxygen demand (BOD). The process involves three stages: anaerobic zone (P), anoxic zone (N), and an aerobic zone (BOD).

Acrylamide, CH2CHCONH2 – The monomer of polyacrylamide which can be toxic to the human nervous system. This form may be present at trace levels in the polymer used for wastewater treatment.

Activated sludge process – A continuous aerobic biological treatment for wastewater using a culture of bacteria that is suspended in the wastewater in an aeration tank. The bacteria adsorb, absorb, and biodegrade the organic materials in the wastewater.

Agricultural runoff – Describes the water that flows from cultivated land.

Agricultural wastewater – Includes liquid runoff from slurry pits or lagoons which are likely to be high in organics and nutrient content. Although it can be beneficial when spread on land for plant growth, it can also be a source of pollution in rural areas.

Algae – large group of simple photosynthetic autotrophic organisms.

Algal harvesting – Algae are grown in a lagoon of wastewater or effluent to reduce the nitrogen and phosphorus concentrations and are removed periodically.

Alum – The commercial grade aluminum sulfate $Al(SO_4)_3$ which is commonly used as a coagulant for water treatment.

Aluminum in water – carry-over of Aluminum from water treatment works can result in significant concentrations in treated water. Aluminum has been linked as a cause of Alzheimer's and can be toxic to fish.

Bardenpho process – An version of the activated sludge process involving five stages so it can reduce biological oxygen demand, remove phosphorus, and achieve nitrification and denitrification.

Biochemical oxygen demand - BOD – A measure of the amount of biodegradable organic substances in water expressed in the mg of O_2 required for microbes to oxidize the organic matter in a liter of the water.

Biological phosphorus removal – BPR – The removal of phosphates from wastewater by incorporation into living matter such as activated sludge.

Bloom – Describes an explosive growth of micro-organisms resulting in a green (can be other colors) mat on the water surface. Blooms can also be associated with unpleasant odors and taste and can create anoxic environments upon death.

Buffering – The property of a substance or system to resist changes in pH.

Carry-over – The failure to remove all of the pollutants in a treatment step resulting in passage of unwanted materials or chemicals.

Chemical treatment – The addition of chemicals to obtain a desired effect.

Clarify – To remove turbidity or suspended solids to increase clarity

Coagulation – The addition of a chemical to form a precipitate that entraps or adsorbs material like suspended colloids.

Denitrification – The reduction of nitrates in anoxic conditions forming gaseous nitrogen which is lost from the wastewater to the atmosphere.

Effluent – Generally describes the fluid or air which flows out after treatment. Here however it is also describing partially processed wastewater.

Erosion – Removal of topsoil by rainfall.

Eutrophic – Description of water which is rich in nutrients.

Eutrophication – The process of becoming eutrophic. P is the key nutrient in freshwater systems that can limit eutrophication.

Floc – grouping of solid particles

Flocculant – A chemical or physical reagent used to promote flocculation.

Flocculation – The grouping of solids in a solution resulting in flocs. The term is often confused with coagulation.

Flocculent – The particles that form flocs.

Irrigation – Artificial water of agricultural land by pipe or by channel.

Lagoon – storage pond for wastewater which can serve many functions.

Methane – CH_4 – A greenhouse gas targeted for reduced emissions formed by the anaerobic degradation of organics.

Organic – Compound containing Carbon to Carbon bonds.

Phosnix process – A method of wastewater treatment using magnesium hydroxide to precipitate and remove phosphorus as struvite (magnesium ammonium phosphate).

Phosphorus – A major essential element for human, animal, and plant growth. Phosphorus is often the limiting nutrient for algal growth in freshwater systems.

Phostrip process – A technique of phosphorus removal using the activated sludge process where the activated sludge is returned to an aerobic tank which releases phosphorus from the activated sludge. The sludge is then sent back to the aeration tank while the phosphorus rich

solution is sent to another tank where lime is added to precipitate and remove the phosphorus in the form of calcium phosphate.

Polyacrylamide – PAM – Organic polymer widely used in wastewater treatment to aid coagulation and flocculation.

Polyelectrolyte – A polymer with ionisable groups that can have positive or negative charges when dissolved in water. Examples: cationic, anionic, and nonionic polyacrlyamides.

Polymer – A substance composed of long chain molecules which are built by linking monomers, simple molecules, together.

Precipitation – 1) Any form of water from the sky. 2) Appearance of white powder or crystals from a solution, often viewed first as cloudiness in the solution.

Runoff – Rain water which runs over the soil surface sometimes detaching soil particles and transporting them.

Sedimentation – settling, sinking, the removal of particles from a solution through the effect of gravity.

Settlable solids – The solids large or dense enough to fall out of a wastewater in the time it is allowed to site in the sedimentation pond or lagoon.

Sludge – Solids which settle out from a wastewater but still contain a high amount of water.

Solubility – mol/L, g/L -The extent to which a material can dissolve in a solvent.

Struvite – Also known as Magnesium ammonium phosphate. It can form deposits on the insides of pipelines containing animal or human wastewater.

Suspended solids – The total solids in a liquid.

University of Cape Town process – UTC – an Adaptation of the activated sludge processes which uses four stages: anaerobic (to remove phosphorus), two anoxic stages (for denitrifcation) and an aerobic stage (for BOD and nitrification).

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Amanda Bragg, daughter of Tom and Sheryl Bragg, was born in Corsicana, TX on May 15, 1980. She graduated from Dawson High School in May of 1998. In May of 1999, she received an Associates of Applied Science from Navarro College. She obtained a Bachelor of Science degree in agronomy from Texas A&M University in December of 2001. She worked for the Texas Cooperative Extension Soil, Forage, and Water Testing Lab from May of 2000 until May of 2002. Upon beginning her M.S. program, she became a graduate assistant for Dr. McInnes in June of 2002.